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DIRECT CONVERSION OF SYNTHESIS GAS TO HIGH OCTANE GASOLINE OVER HZKQ-IB ZEOLITE

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A B S T R A C T

Within the framework of this cost-shared research and development project, a technical feasibility study has been conducted on the direct conversion of synthesis gas into high octane gasoline over a proprietary multi-functional crystalline ironborosilicate zeolite designated as ZKQ-IB, used either in its original hydrogen form or its chemically modified form.

The methods of preparation as well as the characterization of the crystalline ironborosilicate zeolite are described and results obtained therefrom are discussed.

Five base zeolites in the hydrogen form and differing essentially in their total iron contents were synthesized and then each tested in a small fixed-bed reactor for a time on stream of at least 240 hours. On the basis of the test results, which are equally discussed at considerable length, IB-2A base zeolite was selected for longer duration tests and chemical modifications.

Four catalysts prepared by modifying IB-2A base zeolite by ion-exchange with Ni, Co, and La and/or impregnation with Co and La were tested. The results are presented and discussed. The profound effects exerted by the presence of high residual sodium in the H-base zeolites on the one hand and on the other, of the aforementioned transition and rare-earth metals on catalytic activity and selectivity are also described and discussed at length.

In the majority of cases, both modified and unmodified zeolite displayed high synthesis gas conversions and high selectivities to gasoline. However, base zeolite containing relatively high residual sodium content and zeolite impregnated with both Co and La co-produced gasoline and distillate.

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Suggestions are made regarding the potential applications of these crystalline ironborosilicate zeolites to the co-production of premium gasoline, diesel or jet fuel, and the upgrading of primary F-T product hydrocarbons to high octane gasoline.

In view of the highly promising results obtained in this project, five major recommendations are made as a continuation in part of this project.

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1.0 INTRODUCTION

Liquid fuels, because of their ease of handling, constitute the most efficient form of fuel especially in the transportation sector. The supplies of conventional crudes are dwindling rapidly and liquid fuels produced from non-conventional sources such as natural gas, coal and biomass are expected to gain importance in the future.

Several processes have been investigated for the production of liquid fuels from these sources; of those, only two have been commercialized and both involve synthesis gas as an intermediate. The first process developed and exploited for the indirect liquefaction of coal via synthesis gas by the German prior to and during the second world war is known as the Fisher-Tropsch process (1-2). At the height of production in 1943, nine German plants were producing 600,000 tons of hydrocarbons consisting of 46% gasoline, 23% diesel, 28% waxes and 3% lubricating oil. Today, South African Synthetic Oil Ltd (Sasol), operates the only commercial indirect coal liquefaction plants in the world. These plants are believed to meet about 40% of South Africa's motor fuel consumption (3). Even with the most advanced technology used by SASOL, the Fisher-Tropsch (FT) process is not economically competitive with the production of liquid fuels from conventional sources. The major limitation of the FT process is the lack of selectivity for a specific fuel class.

Production costs for a typical Fisher-Tropsch plant processing coal can be broken down as follows (4):

- 58% syngas production
- 18% Fisher-Tropsch synthesis
- 12% product separation
- 10% refinery
- 2% miscellaneous.

Overall, 5% of the process costs could be saved if the production of light hydrocarbons (C1-C4) could be eliminated and over 20% if the selectivity could be contained in the gasoline range.

One process developed to circumvent the selectivity problem presented by FT processes involves the conversion of syngas-derived-methanol into gasoline over shape selective zeolite catalysts such as ZSM-5 (5-7), ABM-1B (8) and ZMQ-TB (9-11). The first commercial plant in the world processing natural gas into gasoline via methanol has been on stream since the early 1986 (12). The plant employs a single train of fixed-bed reactors which are designed to process $4 \times 10^6 m^3$ of natural gas daily into 4840 tons of methanol which are then converted into 14,000 barrels of gasoline (13). Although the Methanol-To-Gasoline (MTG) process is very selective for gasoline, giving yields of the order of 80%, the complexity of this three step process hinders its economic viability. The MTG process requires high capital investment and must be subsidized at the present time.

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A related process which has successfully passed the demonstration stage is the Mobil Olefins-to-Gasoline / Distillate process (MOGD Process) (14). Light olefins which may be obtained from FCC or from methanol are converted to gasoline and/or distillate range products depending on operating conditions. The ratio of gasoline to distillate can be varied from 0.9 to 0.1 to accomodate shifts in demand. Moderate pressures of up to about 10 MPa and relatively low temperatures of 200-250°C are conducive to middle distillate formation over pentasil zeolites of the ZSM-5 type. The distillate produced is highly olefinic and it requires a mild hydrogenation before it can be used as diesel, aviation jet fuel or as a blending stock.

In the U.S. the major multinational corporations such as Mobil Oil and Union Carbide are developing selective catalysts and processes for the direct production of motor fuels from synthesis gas. Mobil's catalysts are based on its proprietary zeolite, ZSM-5. Union Carbide, a major manufacturer of zeolites, has been developing similar catalysts based on silicalite and other zeolites. These cobalt-promoted molecular sieves catalysts produce gasoline and diesel (15-16). In west Germany, Kolbel et al have been pursuing the development of slurry reactor for F-T synthesis and the development of highly selective manganese/ iron-based catalysts for light olefins production directly from synthesis gas (17-18). Japanese workers have recently developed highly active and selective synthesis gas and methanol conversion catalysts within the framework of activities of Japan's Research Association for Petroleum Alternatives Development (RAPAD) (19).

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In this study the use of proprietary zeolite catalysts containing the active metals in the framework has been investigated. The base zeolite has also been modified by impregnation or ion exchange with other promotors in order to maximize the selectivity and conversion yields.

2.0 THE FISCHER-TROPSCH SYNTHESIS

2.1 The basic reactions

The Fischer-Tropsch synthesis has been the subject of several excellent reviews in which the early work has been well covered (6,20-23).

Aside from the occurence of some undesirable side reactions, which will be listed below, the F-T synthesis can be reduced to two fundamental reactions: the first reaction involves the hydrogenation of carbon monoxide in accordance with equation 1 which takes place preferentially on cobalt and nickel catalysts and to a smaller extent on iron catalysts. Water, then, is the primary reaction product. The other reaction is the well-known water-shift reaction represented by equation 2 which takes place most readily on iron catalysts. This reaction changes the oxygen-containing by-products from water to CO_2 and alters the H_2/CO usage ratio. Long contact times of the reacting product on the catalyst surface would increase carbon dioxide formation whereas short contact times would favour the formation of water (24).

$$CO + 2H_2 \rightarrow (-CH_2-) + H_2O \qquad \Delta H_R^{227°C} = -165kJ \ldots (1)$$

$$CO + H_2O \rightarrow H_2 + CO_2 \qquad \Delta H_R^{227°C} = -39.8kJ \ldots (2)$$

$$2CO + H_2 \rightarrow (-CH_2-) + CO_2 \qquad \Delta H_R^{227°C} = -204.8kJ \ldots (3)$$

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The overall reaction represented by equation 3 expresses the synthesis of hydrocarbons on iron catalysts. The heat of reaction liberated during F-T synthesis amounts to about 25% of the total heat of combustion of synthesis gas. The removal of this heat is a major consideration in reactor design.

Both the synthesis reaction and the water shift reaction occur in parallel but at different rates.

The shift reaction affects mainly the H_2/CO usage ratio; the H_2+CO conversion depends mainly on the FT activity. Shift activity has a significant effect on H_2+CO conversion only when it is low. The H_2/CO usage ratio increases with declining shift activity. A high H_2/CO usage ratio leads to a lower H_2/CO ratio in the reactor than in the feed. The H_2/CO in the reactor affects catalyst ageing. The relative activity of FT and shift reactions depends on the nature of the catalyst and the operating conditions used.

Hydrocarbons can also be formed according to equation 4.

$$CO_2 + 3H_2 \rightarrow (-CH_2-) + 2H_2O \quad \Delta H_R 227°C = -125.2kJ \ldots (4)$$

According to equations 1 and 3 the maximum yield of hydrocarbons in a stoichiometric conversion is 208.5g/NM^3 of synthesis gas. The corresponding yields of water and CO_2 are 267.9g and 654.8g respectively.

Likewise, according to equation 4, the maximum yields of hydrocarbons and water are 156.3g and 401.8g respectively. The overall product distribution by weight is ca 30% hydrocarbons, ca 20% water and ca 50% CO_2 in most F-T syntheses (25).

In tests conducted at 7 atmospheres of H_2/CO=1:1 and 100 GHSV H^{-1} on 12 commercial synthetic iron catalysts previously reduced in dry H_2 for 4050 hr at 7 atmospheres of synthesis gas (2:1), the average yield of products per 1000 NL of syngas feed was (6):

WT% H_2O : 5.06
WT% CO_2 : 70.30
WT% $(CH_2)n$: 24.63

Figure 1 shows the carbon balances for different carbon monoxide conversions (24). The H_2:CO ratio used was 2:1 and the operation was carried out in one step with a recycle ratio of 1:1.

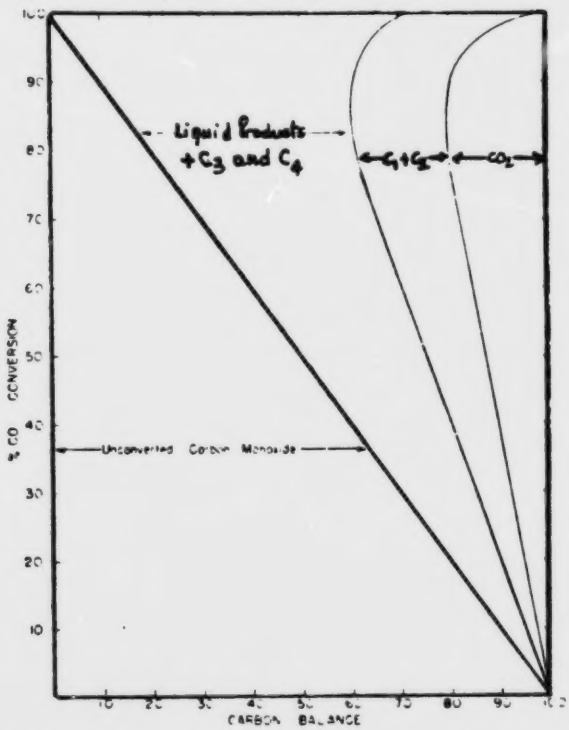

FIG. 1. Carbon balances at different CO conversions (iron catalyst) (24)

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Some of the complicating side reactions which may occur during hydrogenation of carbon monoxide are:

1. Formation of carbon according to the Boudouard reaction:

   $2CO \rightarrow C + CO_2 \quad \Delta H = -172$ kJ/mole
   This reaction is enhanced in the presence of water and other hydrogen - containing compound.

2. Coke deposition:

   $H_2 + CO \rightarrow C + H_2O$

   Carbon formation is mostly connected with the inability of the reactor to remove completely the heat of reaction.

3. Hydrogenation of CO to CH_4 according to the following reactions:

   $CO + 3H_2 \rightarrow CH_4 + H_2O \quad \Delta H = -206$kJ/mole
   $CO + 2H_2 \rightarrow CH_4 + CO_2$

4. Oxidation of the catalyst which depends inter-alia on the CO_2/CO and H_2O/H_2 ratios.

The main technical problems of the F-T synthesis are:

1. The rapid removal of the heat of reaction which amounts to about 25% of the heat of combustion of the synthesis gas;

2. The avoidance of local overheating of the catalyst causing hot spots which favour methane formation and at the same time may cause damage to the catalyst itself;

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3. Maintaining a uniform distribution of the synthesis gas over the catalyst. Non-uniform distribution of synthesis gas over the catalyst occurs particularly in situations where sufficient carbon is allowed to accumulate in the pores or grow in metal crystallites, causing the break up of the catalyst pellets into a fine powder. Consequently, the carbon and catalyst powders can plug the voids, thereby leading to channelling effects with attendant decrease in catalytic activity and the eventual plugging of the reactor (26, 27).

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2.2 Selectivity of Fischer-Tropsch synthesis

The major limitation of classical F-T synthesis is the low selectivity to the desired products. Several transition metals form active FT catalysts; Ni, Co, Fe, and Ru have the most pronounced activities. Of these, Co and Fe have been employed commercially. Considerable interest has recently been shown in catalysts containing the more active but much more expensive ruthenium, which yields polymethylene from synthesis gas. Late transition metals such as copper and palladium are inactive in hydrocarbon synthesis. What differentiates the two groups of metals appears to be their mode of binding CO. Metals active in hydrocarbon synthesis adsorb CO dissociately whereas Cu and Pd, which yield products in which the C-O bond remain intact as in methanol, show only associate adsorption of CO. Another transition metal, manganese, while itself not essentially active in F-T synthesis, appears to exert a major influence on catalyst selectivity. Indeed, the selectivity to lower hydrocarbons could be enhanced by incorporating a second metal in the catalyst which suppresses chain growth and facilitates desorption of short-chain hydrocarbons (28, 29). Catalysts containing iron and manganese can yield products containing up to 80% C_2-C_4 olefins (30).

Usually activated via reduction of its oxide, metal forms the major part of the various catalyst formulations. The other important part of the catalyst is the promotors, which have essentially two functions; metal oxides such as Al_2O_3, MgO, SiO_2, and Cr_2O_3 appear to increase catalytic activity by yielding catalysts of considerably

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higher surface areas. Other metal oxides such as those of the alkali metals seem to exert a profound influence on product selectivity by acting more directly on the active sites. Parameters such as temperature, pressure, composition of synthesis gas, space velocity and alkalization of iron catalysts have been shown to affect chain length, chain branching, ratio of olefins to paraffins, alcohol, carbon and methane selectivity (31). For instance, the presence of potassium in iron catalysts appears to reduce methane formation. Alkali metals reduce the hydrogenating power of the catalyst; increasing the concentrations of alkali in iron catalysts increases the selectivity to olefins and gives products of increased molecular weight. Aside from the above-mentioned parameters, product molecular weight distribution may be controlled via the establishment of a geometric restriction, which involves limiting either the size of the support thereby giving rise to what is commonly known as shape selective catalysis. Inorganic supports such as silica, alumina, various zeolites and the newer SMSI class of supports can influence product selectivity not only by their ability to stabilize metal dispersions but also, where applicable, by their geometric properties (32-35).

The dependance of selectivity on catalyst particle size has been demonstrated by various workers who prepared highly dispersed metal catalysts by impregnating inorganic supports with metal complexes or clusters (36-41).

Iron-based F-T catalysts are relatively inexpensive. Their ability to yield a spectrum of products which is by far more complex than that obtained from cobalt or

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nickel, makes them commercially interesting for the synthesis of motor fuels. According to Dry (42) there is a simple relationship between the selectivities for products of various carbon numbers. Thus, if the selectivity to any one particular carbon number species is changed, the selectivities to all other products will also change by a predictable amount, irrespective of the manner by which the selectivity changes have been effected. There is, therefore, an interdependence of selectivities, as illustrated in Figure 2.

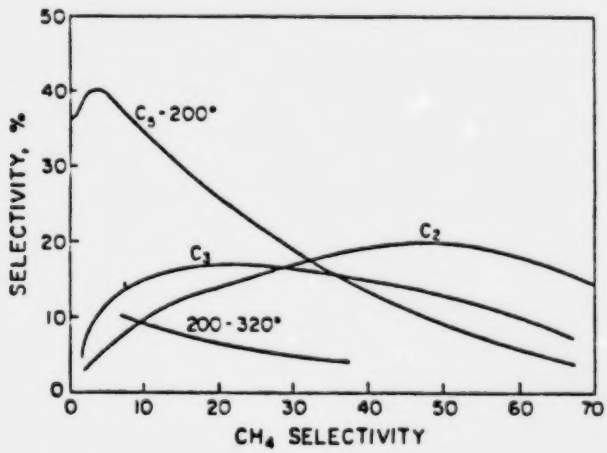

FIG. 2. The interdependence of the product selectivities with Fischer-Tropsch catalysts [42]. Data are the average for a variety of SASOL Fe catalysts at 200-340°C, 5-40 atm.

On the basis of detailed analysis of products from iron catalysts, Pichler et al (43) have shown that when process conditions and catalyst composition are altered, changes are observed in both the overall carbon number distribution and the types of compounds present in the different cuts. For instance, at 320°C, a general decrease in the olefinicity of the products is observed as the carbon number increases; at 200°C, such a trend was not observed. At a synthesis temperature of 220°C, the products are mainly

straight chain with low amounts of aromatics and branched compounds. As the temperature is increased from 220°C to 320°C, there is a general increase in the degree of branching and aromaticity of the products (44). In general, as the synthesis temperature is increased the product selectivity shifts to lower molecular weight compounds. Briefly the broad product distributions associated with classical F-T synthesis depend inter-alia on such variables as the nature of the metal and the support if any, reaction temperature and pressure, feed-gas composition, and the nature of the promotors.

The synthesis of hydrocarbons from CO and H_2 on a classical F-T catalyst can be regarded as starting from an initial C_1 unit which gradually grows to yield higher hydrocarbons. In competition with this growth process is the termination process which involves desorption of the hydrocarbon chain from the catalyst surface into the gas phase as product. This growth process may be explained by a polymerization mechanism in which the growth of hydrocarbon units takes place predominantly in single-carbon additions. Statistically speaking, the growth process and the competing termination process each has certain probabilities which are independent of the size of the hydrocarbon unit attached to the catalyst surface.

On the basis of extensive experimental data and assuming that all surface units are equally reactive for chain growth and product desorption are constant, it has been found that the growth process by a polymerization mechanism can be adequately defined by a most

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probable distribution function, which is identical to the Schulz-Flory distribution function used to describe polymerization processes (45). This function is identical also to that derived by Storch et al (6) to describe F-T synthesis data in the absence of chain branching. This mathematical function, which predicts the product distribution as a function of carbon number n, is expressed in the form of equation (5),

$$\ln W_n/n = n \ln P + \ln (1-P)^2/P \quad \ldots\ldots\ldots (5)$$

wherein W_n is the weight fraction of the product of carbon number n, and P represents the probability of chain growth. The reciprocal of (1-P) gives the degree of polymerization, D. A plot of W_n/n versus n should give a straight line whose slope and intercept give the same value of P, provided this distribution function applies. Industrial F-T data are in agreement with the Schulz-Flory distribution as is evident from figure 3 (33). This, then, lends strong support to the proposed model of chain growth.

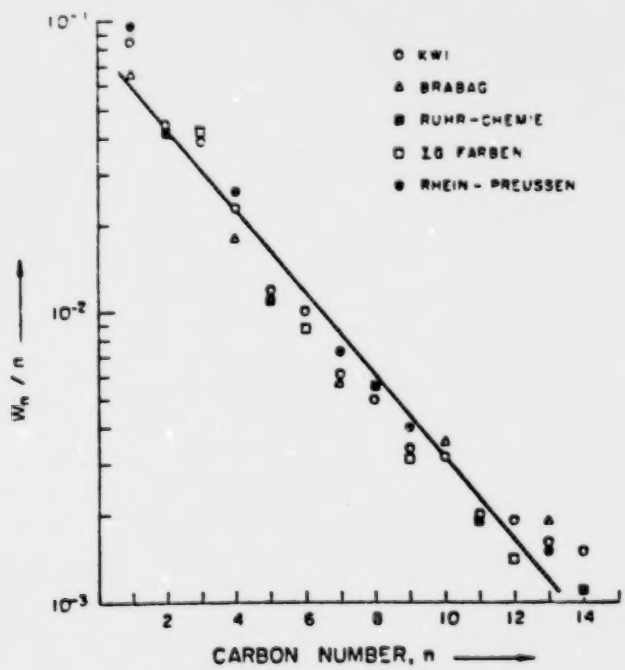

FIG. 3. Hydrocarbon distributions for commercial iron catalysts plotted according to Eq. (5). Ref. 33

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According to equation (5), the entire product distribution is determined once P is fixed. Thus, the Schulz-Flory polymerization process imposes selectivity constraints in CO-H_2 reactions. As can be seen in Figure 4 where W_n is plotted as a function of the degree of polymerization, D, the maximum attainable selectivity to gasoline boiling range products is about 47%, whereas that for C_2 hydrocarbons for example, is roughly 30%. As has been borne out in practice, only in the case of C_1 compounds such as methane and methanol can a 100% selectivity be achieved.

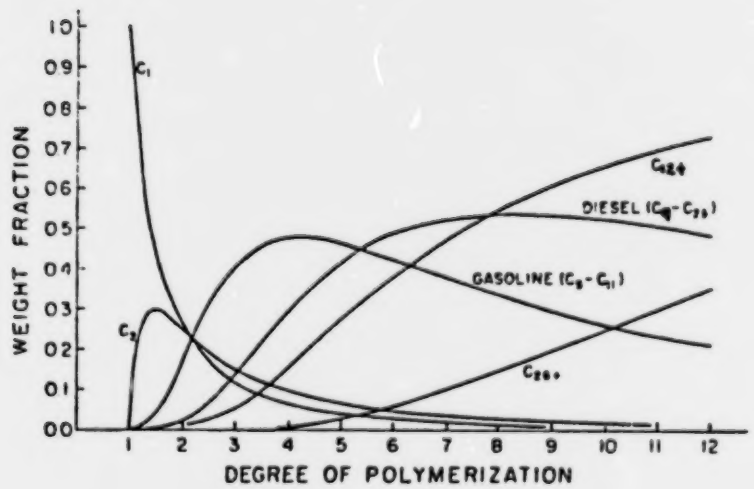

FIG. 4. Selectivity limitations on Fischer-Tropsch synthesis as determined by the Schulz-Flory distribution function. Ref. 83

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The consequence of the selectivity limitations on F-T synthesis is higher production costs due to costly product separations and upgrading of lower-grade fractions.

2.3 Circumventing the selectivity limitations in H_2-CO reactions

During the rather long history of Fischer-Tropsch synthesis, several approaches have been pursued in an attempt to circumvent the selectivity constraints to which it is subjected. King et al (33) have divided these approaches into four distinct categories:

1. Limitation of chain growth by pore size.
2. Interception of surface intermediates during F-T synthesis
3. Modification of Fischer-Tropsch catalysts.
4. Development of catalysts which function by mechanisms that are not selectively - limited by a Fischer-Tropsch polymerization mechanism.

In this section we shall deal only with the interception of surface intermediates during synthesis since this concept appears to underline the mode of action of ZKQ-IB during synthesis.

Research and development in the field of liquid synthetic fuel derived from synthesis gas has mainly

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centered on the development of highly selective catalysts that maximize yields of gasoline and/or middle distillates, and on the development of processes that fully exploit the capabilities of the newly developed catalysts. Substantial progress has been made in the area of synthesis gas conversion catalyst development in the wake of the discovery by workers at Mobil Research Laboratory of the ZSM-5 catalyst, a medium-pore synthetic zeolite possessing shape-selective properties which can convert methanol to a mixture of aliphatic, alicyclic, and aromatic hydrocarbons in the gasoline boiling range (9,46-48). This landmark discovery has led to the development of bifunctional or multifunctional conversion catalysts, which essentially comprise:

- a mixture of a F-T active transition metal or its oxide and an excess of a pentasil zeolite such as H-ZSM-5 or silicalite (56-65);

- a mixture of a methanol synthesis catalyst and an excess of a pentasil zeolite such as H-ZSM-5 (59-60);

- either a crystalline transition metal silicate or a transition metal borosilicate which is an analogue of ZSM-5 (4,61-63);

- loading ZSM-5 type zeolites with transition metal organic complexes or vacuum impregnating with metal salt solutions (64-67).

The approach pursued by CRIQ in this regard has been the development of synthetic crystalline ironborosilicate pentasil zeolites designated as ZKQ-IB. In

contrast to catalysts comprising of an intimate blend of F-T or methanol synthesis catalyst with an excess of a shape selective molecular sieve, all of the functional elements of ZKQ-IB are part and parcel of its crystalline zeolitic structure in which they are incorporated during hydrothermal crystallization by partially substituting for silicon and/or by reacting with silicic acid. This proprietary zeolitic material does not contain segregated crystalline phases of oxides of iron on the basis of x-ray diffraction results. Iron and boron impart F-T function and acidity respectively to ZKQ-IB, which possesses shape-selective properties analogous to those of ZSM-5 by virtue of its inherent crystalline structure.

According to current thinking, the mode of operation of multifunctional catalysts comprising an active F-T metal and a shape-selective zeolite or a crystalline pentasil metal silicate zeolite is based on the interception of low molecular weight intermediates or primary products arising from $CO-H_2$ synthesis reaction before the normal polymerization process takes place. Subjected to a "drain-off" action by the zeolite that overcomes thermodynamic equilibrium, these low-molecular weight intermediates are converted in good yields mostly to liquid hydrocarbons in the gasoline boiling range (68-69). If the active F-T component is replaced by a methanol synthesis catalyst, methanol, which is the primary product formed, will be converted to gasoline by the well-known mechanism invoked in the MTG process. This mechanism appears to be similar to that proposed for the conversion of intermediates arising from "controlled F-T synthesis" in view of the similar product distribution. As expected, the

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product spectrum is restricted to below C_{11} due to the cut-off of high-boiling hydrocarbons by the zeolitic component. The catalyst produces a wax-free liquid product comprising a mixture of paraffins, olefins, naphtenes, and aromatics. If silicalite constitutes the zeolite component, the liquid product may be devoid of aromatics in view of the fact that pure silicalite does not possess the acidic properties necessary for aromatization of low-molecular weight intermediates or primary products.

Another approach taken to limit the selectivity to the gasoline range involves using two reactors in series rather than a catalyst blend in a single reactor.

Thus, by using a second reactor charged with the H-form of pentasil zeolites such as ZSM-5 (70-74), AMB-1B (75, 76), ZMQ-TB (77), it is possible to upgrade the product effluent from a conventional F-T reactor in a way that ensures production of a better quality gasoline and distillate fuels. The main advantage of such an approach lies in the fact that both reactors can be run separately at their respective optimum operating conditions. Moreover, it makes it possible to regenerate separately the spent catalysts. This is in contrast with multi-functional catalysts which are usually run at temperatures considerably below the optimum temperature at which the zeolite component is normally run. This temperature limitation is brought about by the need to reduce the production of methane and carbon dioxide and prevent the premature deactivation of the metal component in particular. The optimum running temperature of the metal component is normally below the temperature at which the multi-component catalyst is operated.

3.0 EXPERIMENTAL SECTION

The experimental part of the project called for the syntheses and characterization of a number of ZKQ-IB crystalline ironborosilicate zeolites differing mainly in their respective iron contents, the screen testing in a semi-micro fixed-bed reactor of each zeolite continuously over a period of not less than one week, the chemical modification of the most promising catalyst preparation by techniques known in the art and the testing of the modified catalysts. Following the testing of these modified catalysts, the most promising unmodified catalyst and its modified counterpart were each to be tested in a 200 mL modified Berty reactor over longer periods of time in the Fischer-Tropsch Synthesis laboratory at Queen's University.

3.1 Synthesis of ZKQ-IB

ZKQ-IB is a crystalline synthetic ironborosilicate zeolite belonging to the pentasil family of zeolites. It may be represented empirically by formula I given below and expressed in terms of mole oxide ratios.

$$0.9 \pm 0.2\ M_{2/n}O:\ (a\ Fe_2O_3:\ b\ B_2O_3):\ y\ SiO_2.zH_2O \quad \ldots\ldots I$$

Wherein M is a cation of valence n such as that of the alkaline or alkaline earth metal, a and b are each greater than zero but less than 1 such that a+b=1, y is equal to or greater than 4, and z is a number which can assume a value of 0 to 150 or more.

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The precursor of ZKQ-IB, which is often written as (M,TPA)-ZKQ-IB, may be represented by formula II given below and expressed equally in terms of mole oxide ratios.

$$0.9\pm0.2(xR_2O+(1-x)M_{2/n}O):(aFe_2O_3:bB_2O_3):ySiO_2.zH_2O \quad \text{...II}$$

M is a cation of valence n, R is a tetraalkylammonium cation such as that of tetrapropylammonium, x is a number greater than zero but less than 1, and the other coefficients have the same meanings and values as in formula I.

It is generally considered that the formation of synthetic zeolites is favoured by low temperature hydrothermal conditions with concurrent low autogeneous pressure at saturated water vapour pressure. Furthermore, a high degree of supersaturation of the gel components is highly desirable since it leads to the nucleation of a large number of crystals. During the synthesis of ZKQ-IB, the gelling of the reaction mixture is the direct result of the combined effects of the added mineralization agent and tetrapropylammonium bromide and of the reaction between the silica and boron and iron. The high pH of the reaction mixture tends to counteract these effects. A number of interrelated processes such as clathration, nucleation, precipitation and dissolution of particles take place in the reaction mixture.

3.1.1 Method of preparation of ZKQ-IB

A general outline of the method of preparation of ZKQ-IB crystalline ironborosilicate zeolite is given below.

It may be prepared by the method which comprises:

(1) preparing a mixture consisting of the integral reaction products formed between an iron-containing compound and an alkaline tetrahydroborate, a source of silicon, an alkylammonium cation or a precursor thereof, an alkali hydroxide, optionally a mineralization agent, and water;

(2) maintaining the gelled alkaline mixture under autogeneous pressure in an autoclave at a reaction temperature of 158°C for a period of time (usually a week) sufficient to effect hydrothermal crystallization of the ironborosilicate precursor, (M,TPA)-ZKQ-IB;

(3) separation of the ironborosilicate precursor from the mother liquor by filtration or centrifugation followed by washing with deionised water until free of soluble salts;

(4) calcination of the washed product in air at a temperature of 500°C for at least 5 hours to remove the clathrated tetraalkylammonium cation with the resulting formation of the M,H form of ZKQ-IB;

(5) exchanging the calcined material with ammonium cations (5M NH_4Cl) at least twice at 95°C for a period of at least 5 hours, followed by a final washing with deionised water to remove soluble salts;

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(6) Calcining the exchanged material at 538°C in air for at least 5 hours to yield the hydrogen form of the zeolite, that is HZKQ-IB.

The hydrogen form of ZKQ-IB is particularly suitable in synthesis gas or methanol conversion to premium gasoline and in various hydrocarbon conversion reactions. It can be exchanged or impregnated with catalytically active metal ions, mixed with active metal or its oxide or composited with a variety of binders.

Suitable commercially available sources of silicon are Nalcoag 1030™, Ludox-30™, and O Brand sodium silicate. Nalcoag 1030™, which was exclusively used to prepare ZKQ-IB zeolites, is a colloidal dispersion of non-agglomerated spherical silica particles in water. These particles normally bear negative charges, which are stabilised by counter-ions so as to provide a system in equilibrium. There are on the surface of the colloidal particles silanol groups (-Si-OH) which are partially ionised but which can be neutralised by sodium ions. Removal of trace impurities of aluminium in Nalcoag 1030™ is effected by treatment with a strong acidic synthetic polystyrene crosslinked with divinyl benzene resin such as Rexyn-101(H). The specifications of Nalcoag 1030™ are given below.

Wt% colloidal silica	30
Wt% Na_2O	0.40
pH	10.2
Viscosity at 25°C, cps	less than 5
Specific gravity at 20°C	1.205
Average specific area, m^2/g	190-270
Average size of particles, mμ	11-16
Cloud point, °C	4.4

A readily available alkaline tetrahydroborate is sodium tetrahydroborate which serves both as a reducing agent and the unique source of boron in the synthesis of ZKQ-IB. It can be purchased in bulk as a 50% stabilised solution in water. One example of a source of alkylammonium ions is tetrapropylammonium bromide or hydroxide (TPA.Br or TPA.OH). It can also be generated in situ during the hydrothermal synthesis of ZKQ-IB by incorporating in the reaction mixture stoichiometric amounts of n-bromopropane and tri-n-propylamine. The reaction between the latter two liquid compounds is favoured when conducted in methyl ethyl ketone. The optional mineralization agent used in the preparation of ZKQ-IB is sodium chloride. Any water soluble inorganic iron compound may be used as a source of iron. We have used hydrated ferric ammonium sulphate.

The mixture obtained prior to hydrothermal treatment can be characterized in terms of mole oxide ratios of the starting reactants, as shown in Table 1, wherein R, M, and n have the same meanings as in formulae I and II given above.

TABLE 1

RANGE OF MOLE OXIDE RATIOS OF STARTING MATERIALS

Mole oxide ratios	Range of values
$SiO_2/(Fe_2O_3 + B_2O_3)$	4-400
OH^-/SiO_2	0.1-2
$R_2O/(R_2O + M_{2/n}O)$	0.2-0.97
H_2O/OH	10-500

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When an alkali metal hydroxide such as NaOH is used in the zeolite preparation to provide a source of sodium ions for establishing electrovalent neutrality and to adjust the pH of the reaction mixture to the desired value, the range of values of OH^-/SiO_2 given in Table 1 should render the pH of the mixture within the range of 9.5 to 13.5. A pH of between 10.0 to 11.5 is to be preferred as it favours the incorporation of iron and boron in the crystalline framework of the zeolite. pH values greater than about 13.5 appears to be conducive to the formation of mixed crystalline phases wherein allotrophs of silica are often present; pH above 13.5 is therefore not recommended for the preparation of ZKQ-IB. The presence of mixed crystalline phases such as in the case of zeolite/cristobalite normally reduces catalytic activity, BET surface area, and degree of crystallinity of an otherwise pure ZKQ-IB. Furthermore it may interfere with intracrystalline diffusion of reactants and degrees of products from the catalyst surface.

As can be inferred from Table 1, each of the reactants must be added in an amount calculated to give the desired molar composition in the resulting mixture. For instance, by regulating the amount of boron expressed as B_2O_3 and iron expressed as Fe_2O_3 in the reaction mixture, the $SiO_2/(B_2O_3 + Fe_2O_3)$ molar ratios can be made to vary within the range set in the Table. Experience has shown that not all of the added boron and iron are incorporated in the crystalline structure of the zeolite. In particular, the amount of boron incorporated appears to reach a limiting value. This observation is based on the analytical results.

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3.1.2 Preparation of ZKQ-IB zeolites

Several crystalline ironborosilicate zeolites in the hydrogen form, differing principally in their iron contents were prepared in accordance with the method outlined above save for ZKQ-IB1B, which was prepared with boric acid as the source of boron instead of sodium tetrahydroborate. A detailed description of the preparation procedures of ZKQ-IB zeolites is given in reference (11c). The mole oxide ratios of the various starting materials used in the preparation of each of the crystalline ironborosilicate zeolites are given in Table 2, along with the pH of each of the reaction mixtures prior to autoclaving. It is worth noting that in computing the $Na_2O/(TPA)_2O$ molar ratios, the sodium arising from the addition of the mineralization agent, NaCl, and of sodium tetrahydroborate was not taken into account.

TABLE 2
SYNTHESES OF ZKQ-IB IRONBOROSILICATE ZEOLITES
MOLE OXIDE RATIOS OF STARTING MATERIALS

CATALYSTS	$\frac{SiO_2}{B_2O_3}$	$\frac{SiO_2}{Fe_2O_3}$	$\frac{SiO_2}{(B_2O_3+Fe_2O_3)}$	$\frac{OH^-}{SiO_2}$	$\frac{(TPA)_2O}{(TPA_2O+Na_2O)}$	$\frac{Na_2O}{(TPA)_2O}$	$\frac{TPA}{SiO_2}$	$\frac{H_2O}{OH^-}$	$\frac{H_2O}{SiO_2}$	pH
ZKQ-IB0	18.54	98.33	15.60	0.3071	0.47	1.12	0.27	147.1	45.2	11.3
ZKQ-IB1A	16.10	24.37	9.66	0.3205	0.34	1.96	0.18	92.8	28.9	9.6
ZKQ-IB2A	8.40	20.27	5.94	0.3756	0.32	2.10	0.18	74.1	27.84	10.7
ZKQ-IB3A	8.40	17.51	5.67	0.4382	0.29	2.45	0.18	63.5	27.84	10.5
ZKQ-IB4A	8.40	15.41	5.43	0.5445	0.25	3.05	0.18	51.4	27.84	11.3
ZKQ-IB1B	15.85	24.30	9.59	0.4491	0.29	2.44	0.18	108.45	48.71	9.8

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All of the moist zeolite precursors were initially pale grey in colour. Upon prolonged exposure to the atmosphere they gradually assumed a darker shade verging on dark green. This suggests a gradual surface oxidation of Fe^{2+}. Following calcination at 550° C in air, the zeolites were orange-red in colour, indicating the presence of Fe^{3+}.

The base zeolite was modified in the following way:

ZKQIB-2A-Co and ZKQIB-2A-Ni

Both catalysts were prepared by exchanging the base zeolite HZKQIB-2A with a 5% w/v aqueous solution of cobalt or nickel nitrate as the case may be at a temperature of about 90°C for 4 hours. The exchanged zeolite was separated by filtration and washed copiously with hot deionised water. It was dried at 120°C for at least five hours and then calcined in air at 540°C for at least 5 hours.

ZKQIB-2A-La+(Co)

The conversion catalyst was prepared by first exchanging HZKQ-IB-2A with a 5% aqueous solution of lanthanum nitrate hexahydrate at about 90°C for at least 4 hours. Following filtration and copious rinsing with hot deionised water, the exchanged zeolite was dried at 120°C for 5 hours and then cooled to room temperature. It was impregnated with an aqueous solution of cobalt nitrate hexahydrate by the wet incipient method. After drying at 100°C for 4 hours and cooled thereafter to room temperature, it was calcined in air at 540°C for 10 hours. The lanthanum-exchanged zeolite was expected to contain 3% by weight of impregnated cobalt.

ZKQIB-2A-(Co+La)

The catalyst was prepared by impregnating base zeolite HZKQIB-2A with an aqueous solution of nitrates of cobalt and lanthanum by the wet incipient technique. After drying at 100°C for at least 4 hours, the material was calcined at 540°C for at least 10 hours. It was expected to contain 3% and 7.5% by weight of cobalt and lanthanum respectively.

3.2 Characterization of ironborosilicate zeolites

Several analytical techniques were used to characterize ZKQ-IB zeolites. They included:

- classical gravimetry, inducively-coupled plasma spectrophotometry, and spark emission spectrophotometry for elemental analyses; Leco furnace with infra-red detection was used for total carbon analyses;

- powder x-ray diffraction for structure finger printing and for determination of the relative degree of crystalinity;

- BET method for surface area determination;

- Magic angle spinning high resolution NMR of ^{13}C, ^{29}Si, and ^{11}B for structure investigations;

- Thermal analysis for water and TPA^+ determination in ZKQ-IB precursor;

- Adsorption of n-pentane for determination of channel length of unit cell of ZKQ-IB;

- ESCA for surface elemental composition and in particular for surface iron investigation.

3.2.1 Elemental analyses

The elemental constituents of each of the calcined and exchanged zeolites were determined respectively by:

- gravimetry for Si determination;
- spark emission spectrography for boron determination
- inductively-coupled emission spectrophotometry for all other metallic elements
- Leco furnace with infra-red detection of CO_2 for carbon deposit determination.

The results of the elemental analyses provide one with the means to:

- compute the mole oxide ratios, which provide information on the degree of incorporation of boron and iron in the crystalline framework, assuming neither boria nor iron oxide in whatever form are present as a separate phase in the zeolite;

- verify the degree of proton exchange based on the residual sodium concentration in the zeolite;

- determine the concentration of exchanged nickel and cobalt in the zeolite, from which it is possible to estimate the milliequivalents of H^+/g of zeolite.

Shown in Table 3 are the results of the chemical analyses of the calcined ironborosilicate zeolites expressed in terms of weight percent oxides.

TABLE 3

CHEMICAL ANALYSES OF HZKQ-IB ZEOLITES

CATALYSTS	WT %							
	SiO_2	B_2O_3	Fe_2O_3	Na_2O_3	CaO	MgO	OTHERS	LOI*
IB-0A	93.8	0.70	2.85	1.30	n.d	n.d	1.35	1.35
IB-1A	88.1	0.09	8.84	0.30	<0.02	<0.05	2.50	1.46
IB-2A	87.3	0.29	11.50	0.10	<0.02	<0.05	0.69	1.21
IB-3A	82.7	0.32	15.30	0.10	<0.02	<0.19	1.50	1.52
IB-4A	83.8	0.32	15.20	0.72	<0.01	<0.05	0.67	1.46
IB-1B	87.7	0.16	9.96	0.86	<0.02	<0.05	1.16	0.62

* Loss on ignition

REMARK: the result for boria in IB-0A is most probably in error.

The results in Table 3 have been converted in moles of oxides and in mole ratios, as shown in Table 4.

TABLE 4

CHEMICAL ANALYSES IN TERMS OF MOLE OXIDE RATIOS

CATALYSTS	IB-0	IB-1A	IB-2A	IB-3A	IB-4A	IB-1B
SiO_2 (moles)	1.5610	1.4461	1.4528	1.3763	1.3946	1.4595
Fe_2O_3	0.0178	0.0554	0.0720	0.0958	0.0952	0.0624
B_2O_3	0.0101	0.0014	0.0042	0.0046	0.0046	0.0023
Na_2O	0.0210	0.0005	0.0002	0.0002	0.0116	0.0139
SiO_2/Fe_2O_3	87.5	75.83	20.18	14.37	14.65	23.39
SiO_2/B_2O_3	48.2	1032.92	345.91	299.20	303.17	634.57
$SiO_2/(Fe_2O_3+B_2O_3)$	31.0	25.50	19.07	13.71	13.97	22.56
$Na_2O/(Fe_2O_3+B_2O_3)$	0.42	0.0088	0.0026	0.0019	0.1162	0.2093
SiO_2/Na_2O	74.33	2892.2	7264.0	6881.5	120.22	105.0

3.2.2 Preparation of HZKQIB-2A and Ni-ZKQIB-2A for testing in Berty reactor

The modified Berty reactors used in the F-T synthesis laboratories at Queen's University have each a capacity of about 200 mL. In order to meet this requirement in terms of the quantity of catalyst normally tested, two batches of base HZKQIB-2A zeolite were prepared in greater quantities than before by scaling up the amount of starting materials used by factors of

3.5 and 4 respectively. A portion of each of the two batches of zeolite was exchanged with nickel in accordance with the method described above. The results of the chemical analyses for both the base zeolite and the nickel exchanged zeolite are presented in Table 5. The results for boron are not available.

TABLE 5
CHEMICAL ANALYSES OF BASE ZEOLITE AND Ni-EXCHANGED ZEOLITE

CATALYSTS / OXIDES	HZKQIB-2A(3.5)	HZKQIB-2A (4)	Ni-ZKQIB-2A (X3.5)	Ni-ZKQIB-2A (X4)
	WT%			
SiO_2	83.2	83.8	83.6	85.20
Fe_2O_3	13.8	10.9	11.7	9.62
MgO	0.2	<0.05	0.11	<0.05
CaO	<0.02	<0.02	<0.02	<0.02
Na_2O	<0.10	0.33	<0.10	0.33
Others	2.68	4.90	4.47	4.78
Ni	-	-	721 ppm	500 ppm
Zn*	-	-	136 ppm	18 ppm
SiO_2/Fe_2O_3	16.02	20.42	18.98	23.55
SiO_2/Na_2O	865.38	263.13	865.38	267.53

* Zinc contaminant of unknown origin.

3.2.3 Observations based on results of chemical analyses

On the basis of the results of chemical analyses of the base and nickel-exchanged zeolites, the following general remarks can be made:

- in the synthesis of crystalline ironborosilicate zeolites in accordance with the method of preparation outlined above, it is noteworthy that not all of the starting materials are totally incorporated in the crystal framework of the zeolite. In the case of iron, it is estimated that at least 85% of the molar amount of added iron oxide ends up in the protonated zeolite. Whether or not all of this iron in incorporated in the crystal framework is not presently known. More work needs to be done in this area.

- In sharp contrast with iron, the incorporation of boron in the crystal framework is difficult; so is the trace analysis of boron. One important observation is that whatever excess of boron is added to the synthesis mixture prior to hydrothermal crystallization, the amount of boron incorporated in the framework seems to reach a certain limit, which is very small. Based on the semiquantitative results for boron, it appears that, even after making liberal allowance for the rather unprecise results for boron contents, the boria incorporated in the zeolites does not exceeed 1 weight % under the stated reaction conditions. The incorporation of boron is influenced by the pH of the reaction mixture. pH values of about less than 10 appears to be less

favourable to boron incorporation than pH values in the range of 10.5 to 11.5, which range appears to be optimum in light of the results obtained. The acidity of the zeolites would be expected to be low. The "maximum" boron content in the zeolite is estimated to be 0.287 mmole B/g, based on a 1 wt% incorporation of boria. Therefore the cation exchange capacity of the zeolite would be 0.287 mmole of a univalent metal ion such as H^+, Na^+ or K^+ per gram of zeolite, assuming that each boron atom is associated with one cation exchangeable site. In view of the low acidity of the zeolite, it would be expected, for example, that it would have low activity (low conversion) and low aromatization power at moderate temperature (350° C) in regard to the conversion of the methanol to gasoline. HZKQ-IB has been shown to be highly active in methanol conversion and to have moderate aromatization power, which is however less than that of ZSM-5. Furthermore, during previous work, in the presence of synthesis gas, HZKQ-IB has been shown to crack C_{27} to C_{32} wax into gasoline range products. The wax was used as the liquid medium for the slurry reactor in which HZKQ-IB was suspended during F-T synthesis. It appears then that, aside from boron as a generator of acid sites, the other active constituents must also be contributing to the acid properties of the zeolite. This will have to be verified.

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3.2.4 X-Ray diffraction

All of the ironborosilicate zeolites gave x-ray powder diffraction patterns which are similar in all respects. A typical x-ray powder diffraction pattern is shown in Figure 5. Of particular interest is the relative intensities of the two peaks located at 11.2 and 10.05 A. Their intensities are generally lower for zeolite-precursors than those displayed by zeolites that have been calcined. A typical powder diffraction pattern characteristic of all crystalline ZKQ-IB ironborosilicate zeolite is presented in Table 6. Minor shifts in interplanar spacings and variations in relative intensities may occur as a result of ion exchange and of heat treatment; on the whole, however, the diffraction pattern substantially remains the same.

TABLE 6

Typical x-ray diffraction

Interplanar spacings, d (A)	Relative intensity
11.2 ± 0.2	w - s
10.05 ± 0.2	w - ms
9.05 ± 0.15	vw
7.50 ± 0.15	w
7.13 ± 0.15	vw
6.71 ± 0.15	vw
6.40 ± 0.15	w
6.04 ± 0.1	w
5.7 ± 0.1	w
5.60 ± 0.1	vw

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5.13 ± 0.1	vw
5.00 ± 0.1	w
4.62 ± 0.08	w
4.26 ± 0.08	w
4.02 ± 0.08	w
3.83 ± 0.05	vs
3.71 ± 0.05	s
3.65 ± 0.05	m - s
3.43 ± 0.05	w
3.33 ± 0.05	w
3.26 ± 0.05	vw
3.05 ± 0.05	w
2.99 ± 0.02	w
2.86 ± 0.02	vw
2.78 ± 0.02	vw
2.73 ± 0.02	vw
2.61 ± 0.02	vw
2.49 ± 0.02	w
2.39 ± 0.02	vw
2.00 ± 0.02	v - m
1.95 ± 0.02	vw
1.91 ± 0.02	vw
1.87 ± 0.02	vw
1.76 ± 0.02	vw
1.66 ± 0.02	vw

These data were obtained by standard x-ray diffraction techniques, using the K-alpha doublet of copper radiation. In Table 6 the relative intensities are given in terms of the following symbols:

vs.....very strong
s.....strong
ms.....medium strong
m.....medium
mw.....medium weak
w.....weak
vw.....very weak

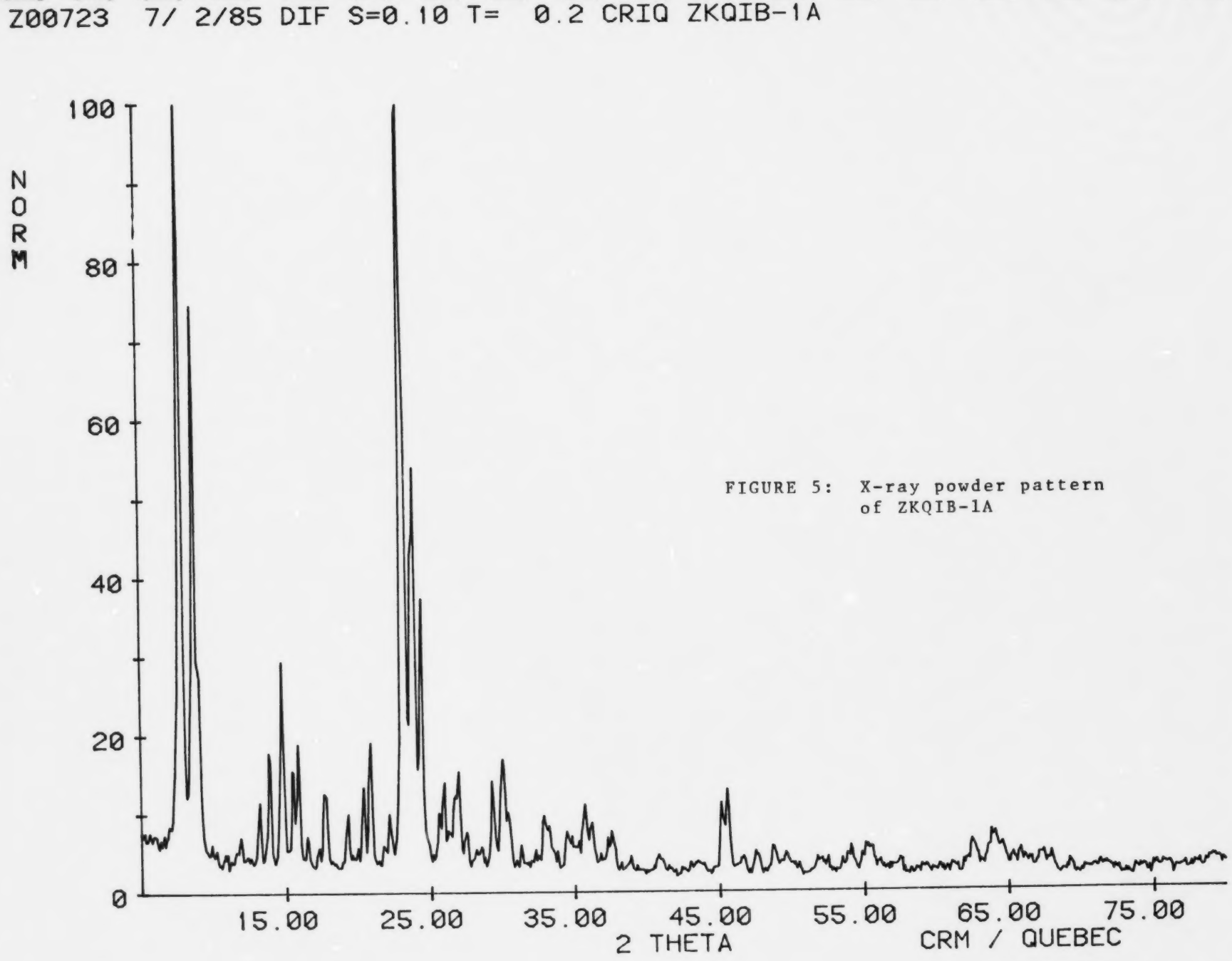

FIGURE 5: X-ray powder pattern of ZKQIB-1A

3.2.5 Relative degree of crystallinity of ZKQ-IB zeolites

The relative degree of crystallinity, which can be determined by x-ray diffractometry, may be defined by the following relation:

degree of crystallinity: $D=(A_s/A_r)x\ 100$

wherein A_s is the total area of the characteristic peaks of the sample located between $2\emptyset_1$ and $2\emptyset_2$ degrees, A_r is the corresponding total area of a highly crystalline reference material whose degree of crystallinity is arbitrarily set at 100%.

In determining the relative degree of crystallinity of ZKQ-IB zeolites, the number of cumulated counts was recorded between $2\ \emptyset_1 = 22°$ and $2\ \emptyset_2 = 25°C$. As seen in any of the x-ray diffraction patterns of ZKQ-IB, highly specific peaks attributed to pentasil zeolite of the ZSM-5 type are located between these 2-theta intervals (78). Some workers chose 22° to 29° as the 2-theta interval. In previous determinations (10) of the relative degree of crystallinity of ZMQ-TB titanoborosilicate zeolites it was found that the zeolite designated as ZMQ-TB5 was the most highly crystallized of all the samples examined. This was found to be equally true for the present determinations. Accordingly, ZMQ-TB5 which is structurally an analogue of ZSM-5 was used as a reference material with a relative degree of crystallinity of 100%. The results obtained are presented in Table 7.

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TABLE 7
RELATIVE DEGREE OF CRYSTALLINITY OF ZKQ-IB ZEOLITES

ZEOLITES	IB-1A	IB-2A	IB-3A	IB-4A	IB-2A(1)	IB-2A(2)	IB-2A1R	IB-2A2R
% CRYSTALLINITY	77.0	82.5	59.1	55.2	88.0	73.1	68.2	70.9

3.2.6 B-E-T Surface area determination

The B-E-T surface area of each of the prepared H-form zeolites was determined on Carol Erba Instruments, an automatic surface area analyser, at ERL, CANMET. The results are shown in Table 8.

TABLE 8
B-E-T SURFACE AERA DETERMINATION

ZEOLITES	IB-0	IB-1A	IB-2A	IB-3A	IB-4A	IB-2A(1)	IB-2A(2)	IB-2A1R	IB-2A2R
BET SURFACE AREA m^2/g	304.7	296.6	306.0	297.0	197.5	240.2	260.9	265.7	289.1

In order to investigate whether or not ironborosilicate zeolites would suffer any change in their BET surface areas and crystalline structure after use, HZKQ-IB5, a zeolite similar in composition to IB-1A which had been tested for 1165 hours under synthesis conditions, was submitted to BET surface area determination and x-ray powder diffraction analysis. Prior to analysis, the carbon deposit was removed by combustion in air. Its B-E-T surface area was 211.9 m^2/g compared to 296 m^2/g before the test. Furthermore, the x-ray diffraction pattern of the coked zeolite was identical to that of the original zeolite, indicating therefore, that the coked zeolite did not suffer from structural changes.

3.2.7 Determination of water and TPA^+ ions in ZKQ-IB precursor

The water and tetrapropylammonium cation contents of pentasil zeolites can be determined by thermal analysis as described in reference (79). The experimental conditions given therein were employed to determine the water and TPA^+ ion contents in only one typical ironborosilicate zeolite precursor such as(Na, TPA)-ZKQ-IBO. The results are presented in Table 9.

TABLE 9
WATER AND TPA^+ DETERMINATION

ZEOLITE	SiO_2/ (B_2O_3+Fe_2O_3)	H_2O per unit cell	TPA per unit cell	Temperature of decomposition °C	
(Na, TPA)-IBO	31	13.7	3.88	1st 430 (16%)	2nd 464 (84%)

The TPA^+ content in the zeolite precursor agrees with published data for ZSM-5 (80). The water content per unit cell of ZKQ-IBO is more than that of titanoborosilicate zeolite, ZMQ-TB. This indicates that ZKQ-IBO is less hydrophobic than ZMQ-TB(3). As seen in Table 9, the TPA ions are of two types: one which is desorbed at higher temperature (464°C) is attributed to those acting as counterious to the framework negative charges; it represents 84 wt% of the total TPA. The other type desorbing at the lower temperature (430° C) and constituting 16wt% of the total TPA is in the form of TPA-OH.

Assuming that the unit cell of anhydrous ZKQ-IB zeolite contains 1 atom of Fe or B, the molecular weight of the zeolite would be approximately between 5800 and 5900.

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3.2.8 Channel length determination of ZKQ-IB by pentane adsorption

Crystalline ironborosilicate zeolites such as ZKQ-IB are hydrophobic in the sense that they sorb greater amounts of simple hydrocarbons such as n-hexane, pentane, cyclo-hexane than water. From a knowledge of the adsorbed amount of pentane for instance, using molecular dimensions and assuming an end-to-end configuration of the adsorbed pentane molecules, it is possible to determine the channel length occupied per unit cell by the adsorbate. n-pentane can completely fill the channel systemof ZKQ-IB. The total estimated crystallographic channel length of ZSM-5 is 8.8 nm; it includes the space at channel intersections, the lengths of the near-circular zigzag and linear elliptical channels (81).

The results of the channel length determination of ZKQ-IBO by n-pentane adsorption are given in Table 10.

TABLE 10
CHANNEL LENGTH OF ZKQ-IBO

ZEOLITE	n-pentane/unit cell	Total channel length/ unit cell (nm)
ZKQ-IBO	9.20	8.25

As has been mentioned above, the total estimated channel length per unit of pure ZSM-5 is 8.8 nm. Given the

structural similarity of ZSM-5 and ZKQ-IB, the difference between this estimated (theoretical) value and that determined for ZKQ-IB which is 8.25 nm, is probably due to the presence of iron and boron in the crystal framework and/or the presence of amorphous phase or mixed crystalline phases. The B-O bond length is shorter than that of the Al-O bond, thus leading to a smaller unit cell dimensions. Indeed, the unit cell dimensions of pure borosilicate zeolites of the ZSM-5 type have been shown to contract linearly with increasing incorporated boron content (82). The reverse is true for ZSM-5 aluminosilicate zeolites; as the aluminium content increases, the unit cell dimensions also increase.

3.2.9 Magic angle spinning ^{13}C-NMR of ZKQ-IB precursor n-propyl group of TPA^+

During the synthesis of zeolites in which organic templates are used, the template cations being structure directing are clathrated and become stabilised in the zeolite channels during hydrothermal crystallization to yield ultimately the crystalline zeolite precursor.

The position and configuration of TPA^+ ions in ZSM-5 precursors can be determined by high resolution magic angle spinning ^{13}C-NMR (21,22). In view of its close structural similarity with ZSM-5, the same technique could be applied to ZKQ-IB. Indeed, it was possible to obtain ^{13}C-NMR spectra of ZKQ-IBO precursor, i.e Na, TPA-ZKQ-IBO, on a Bruker CXP-200 spectrometer.

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The values of the chemical shifts and of the widths of the peaks of the carbon atoms, C_1, C_2, C_3 of the N-propyl group of TPA^+, i.e $N-C_1-C_2-C_3$ are presented in Table 11.

TABLE 11

HRMAS ^{13}C-NMR OF N-PROPYL GROUP OF TPA

CHEMICAL SHIFTS (ppm)			PEAK WIDTHS (Hz)		
dC_1	dC_2	dC_3	ΔH_{C1}	ΔH_{C2}	ΔH_{C3}
63	16.3	11.5 10.2	160	120	120

First and foremost, the NMR spectrum shows that as an occluded species, the TPA ion remains intact in the zeolite, the values of the chemical shifts as well as the splitting of the peak attributed to C_3 indicate that the TPA^+ cation is located in two surroundings. The values of the peak widths imply that the TPA^+ ions are less strongly bound to the zeolite framework that those in ZMQ-TB (10) whose corresponding peak widths are ΔH_{C1}=60Hz, ΔH_{C2}=50Hz, and ΔH_{C3}=120 Hz. The wider the peak, the weaker will be the link between TPA^+ and the zeolite framework.

3.2.10 High resolution MAS ^{29}Si NMR

A high resolution magic angle spinning ^{29}Si NMR spectrum of ZKQ-IBO was obtained on a Bruker CXP-200 spectrometer operating in the Fourier transform mode. It shows essentially the following characteristics:

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- a broad band at -102.9 ppm (from TMS) which is characteristic of silanol groups, Si-OH of ZSM-5 type zeolite (85, 86);

- a resonance centred at -112 ppm with three principal shoulders, one of which is at -117 ppm.

The position and the width of this resonance peak are characteristic of a pentasil type zeolite with probably Si(OB) and Si(OFe) configurations in various geometries.

3.2.11 Solid state ^{11}B NMR

Solid state boron-11 NMR spectroscopy has proved to be very useful for analysing the environment of boron, especially in the crystal framework of pentasil zeolites. It is possible by this technique to identify and differentiate boron incorporated in the crystal framework from boron that is impregnated or mixed with a zeolite. Moreover, it is possible to verify the presence or absence of tetrahedrally-coordinated boron within or without the crystal framework and of trigonally-coordinated boron such as in B_2O_3.

A high resolution magic angle spinning boron-11 NMR spectrum of ZKQ-IB was obtained on a Bruker CXP-200 spectrometer according to the operating conditions described in reference (87). Chemical shifts were measured from BF_3/ether. It showed only one narrow peak of 135 Hz width located at -3.6 ppm, as shown in Figure 6. The line shape indicates that boron is tetrahedrally-coordinated in ZKQ-IBO. The narrow peak is attributed to the relative isolation of boron in

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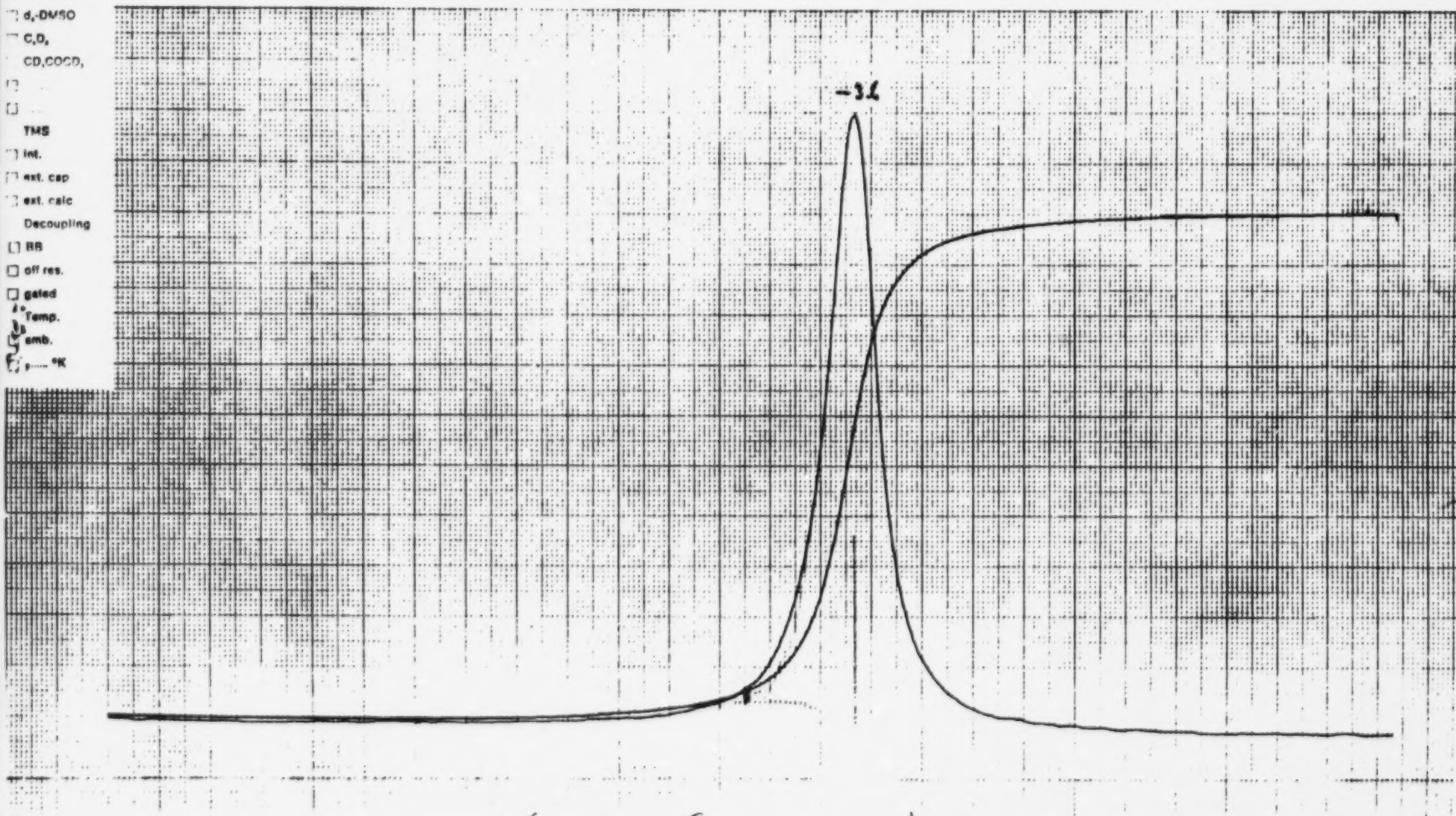

FIGURE 10: MAS "B NMR

the zeolite framework, as compared, for instance, to the relatively broader signal of tetrahedrally-coordinated boron in boron phosphate wherein the boron concentration is much higher than in ZKQ-IBO. In BPO_4 the broadening of the boron resonance signal with a half-width of 2.8kHz is a consequence of the much stronger dipole-dipole interaction (88). Of particular interest is the absence of boron in tetrahedral configuration without the zeolite framework and of trigonally-coordinated boron such as in boria. Futhermore, the absence of a residual peak at -0.5ppm is a clear indication of the highly crystallized state of ZKQ-IBO.

3.2.12 Electron microscope examination of ZKQ-IB zeolites

The electron photomicrographs shown in figures 7a, 7b, 7c are those of ZKQ-IB2A zeolite. They are typical of ZKQ-IB zeolites. They were taken on a JEOL scanning electron microscope at an accelarating voltage of 35 kV. As can be seen in the scanning electron photomicrographs, the near spherial particles have dimensions in the range of approximately 1 micron to about 8 microns. These particles are a product of the agglomeration of lathe-shape crystals and of disc intergrowth (99).

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FIGURE 7a

SCANNING ELECTROPHOTOMICROGRAPH OF ZKQIB-2A

(x 2000)

Scale: 1 micron = 2 mm

FIGURE 7b

SCANNING ELECTRON PHOTOMICROGRAPH OF ZKQIB-2A

(x 6000)

Scale: 1 micron = 5 mm

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FIGURE 7c

SCANNING ELECTRON PHOTOMICROGRAPH OF ZKQIB-2A

(x 10 000)

Scale: 1 micron = 10 mm

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3.2.13 X-Ray photoemission spectroscopy (XPS) or ESCA

The following three ZKQ-IB samples were submitted to the Surface Science Laboratory of the University of Western Ontario for examination by XPS:

a) The first sample designated as HZKQ-IB5 was "heavily" coked during a synthesis reaction run in a modified Berty reactor which lasted about five weeks;

b) The second sample designated as ZKQ-IB1 was actually a precursor to the zeolite. It still contained clathrated or occluded TPA ions; it was an almost white powder;

c) The last sample designated as HZKQ-IB1 was an orange red powder obtained after ammonium exchange and calcination of Na, H-ZKQ-IB1;

All measurements were made on hard discs prepared from the zeolite samples. The equipment used was a SSL SX100 X-ray Photoemission Spectrometer. The surface composition of each of the samples is given in Table 12.

TABLE 12

SURFACE COMPOSITION OF ZKQ-IB ZEOLITES

ZEOLITES ELEMENTS	ZKQ-IBI		HZKQ-IBI		ZKQ-IB5	
	B.Energy (eV)	Atom %	B.Energy (eV)	Atom %	B.Energy (eV)	Atom %
Fe P	708.1	0.58	710.1	0.87	709.1	0.49
O 1S	528.4	40.10	531.4	52.13	531.4	38.21
Na A	493.2	1.05	-	-	-	-
N 1S	398.5	1.05	-	-	-	-
C 1S	281.4	21.93	284.3	14.58	283.3	38.67
C 1S	284.9	13.58	-	-	-	-
B 1S	-	-	192.5	0.98	-	-
Si 2P	99.7	21.70	102.7	31.45	102.7	22.62

The Fe(2P) XPS spectra of ZKQ-IB1, HZKQ-IB1, and HZKQ-IB5 are shown in Figures 8, 9 and 10 respectively. The $2P_{3/2}$ peaks by each of the samples are reported in Table 13.

TABLE 13

Fe(2P) XPS spectra of ZKQ-IB zeolites

ZEOLITES	ZKQ-IB1	HZKQ-IB1	HZKQ-IB5
B.Energy (eV)* $Fe2P_{3/2}$ peak	712	711.1	711.3

*Corrected for charging.

FIGURE 8 : Fe2P x PS spectrum of ZKQ-IBI

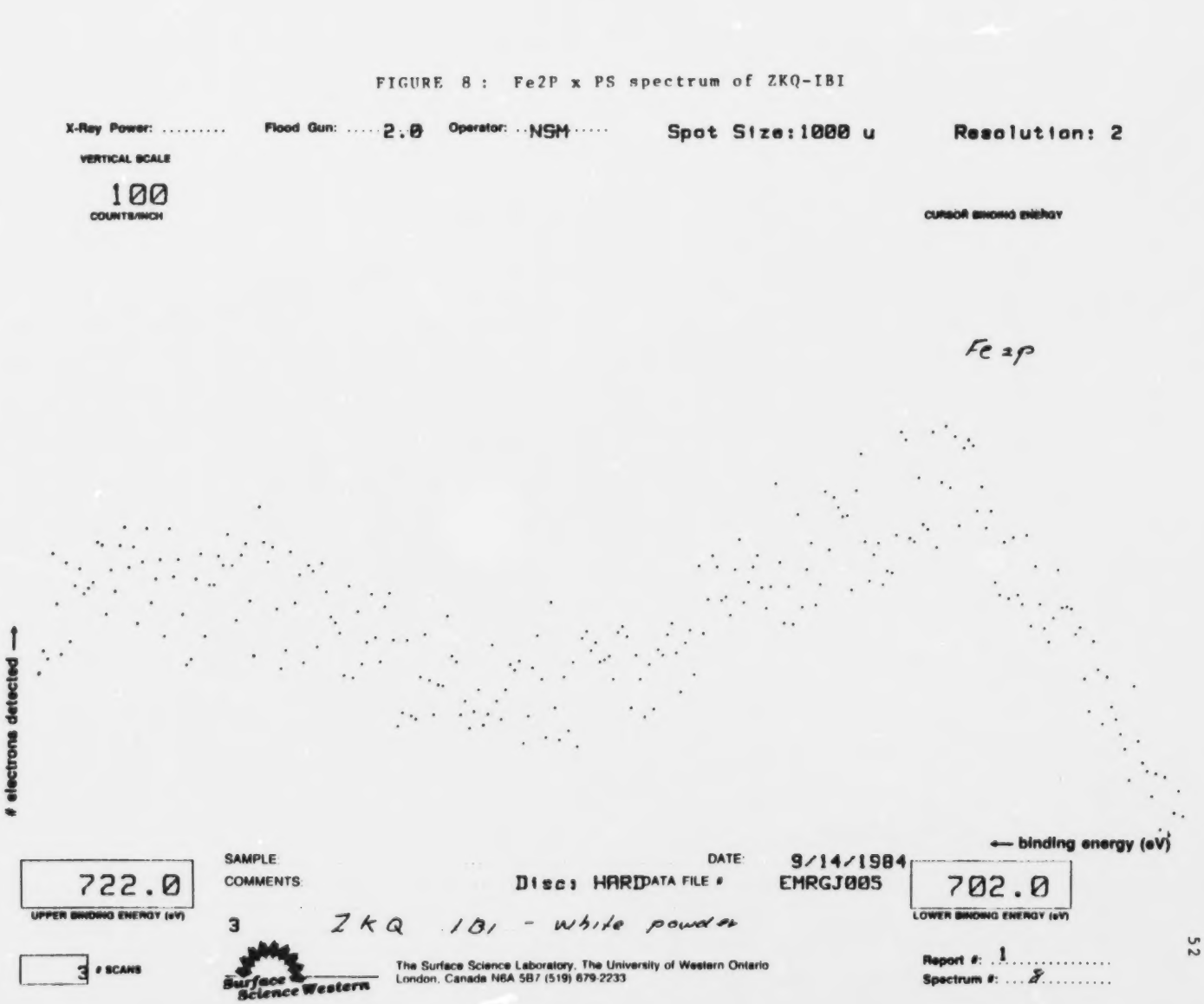


FIGURE 9 : Fe2P x PS spectrum of HZKQ-IBI

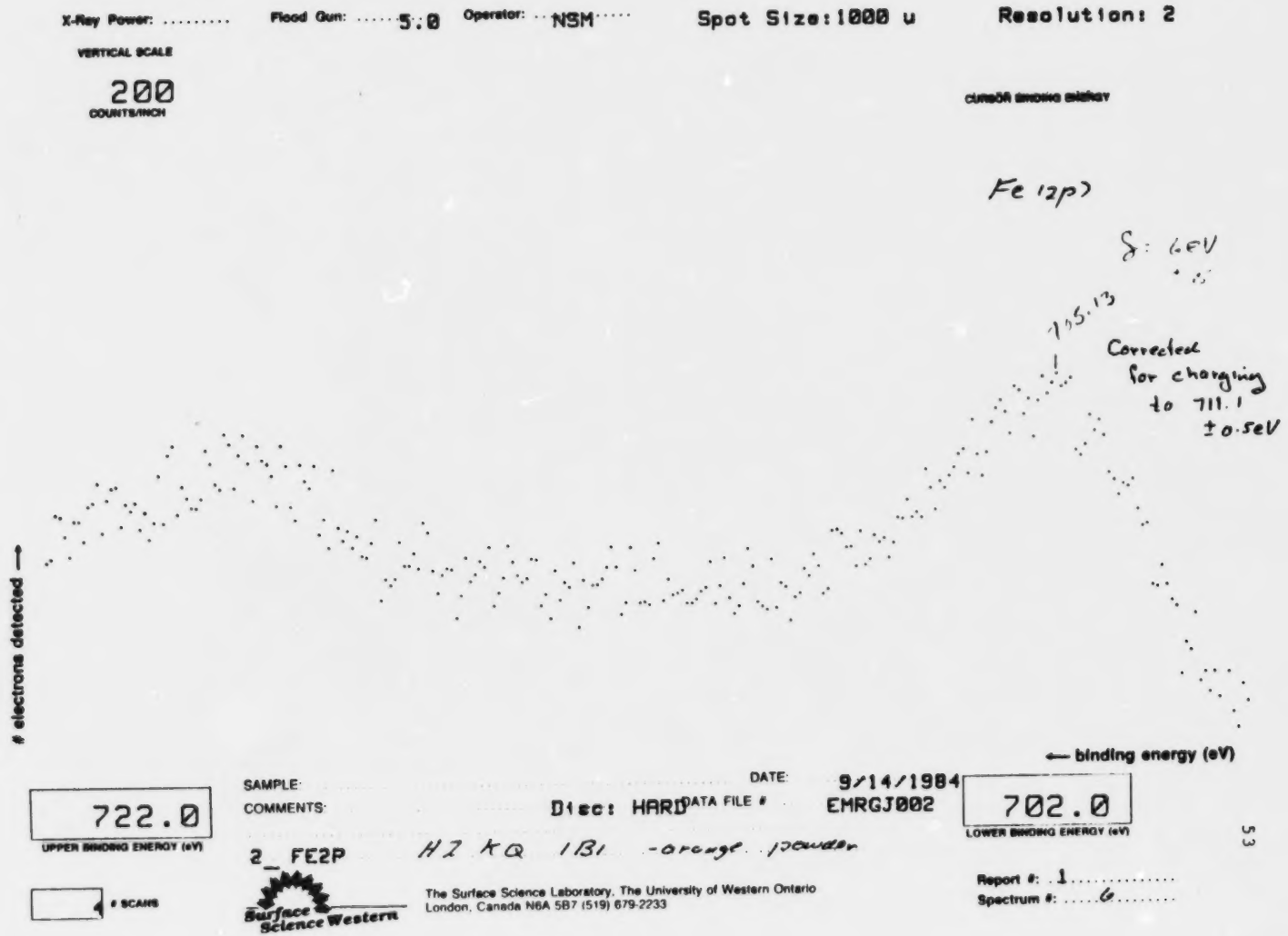
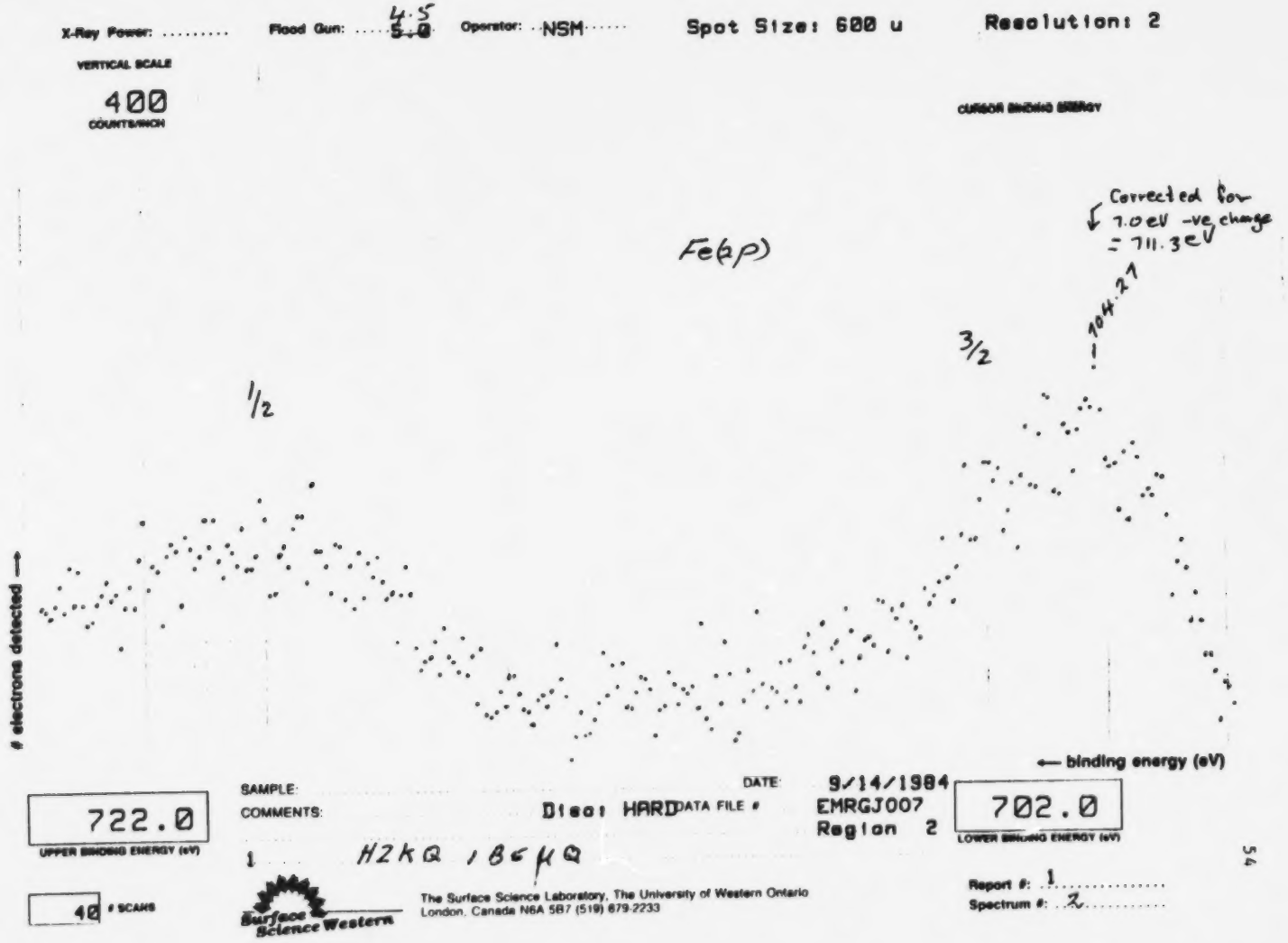


FIGURE 10: Fe2P x PS Spectrum of HZKQ-IB5



A comparison of the surface compositions of the precursor ZKQ-IB1 and its hydrogen form, HZKQ-IB1, shows that:

- surface boron is only present on HZKQ-IB1; this seems to imply that boron is brought to the surface either by ion exchange and/or calcination.

- no nitrogen is detected on HZKQ-IB1, which indicates that TPA ions occluded in ZKQ-IB1 precursor have been completely decomposed by calcination at 538°C. The presence on HZKQ-IB1 of carbon, however, seems to imply that the calcination temperature of 538°C and/or the duration of calcination of 10 hours are not sufficient to remove the carbon resulting from the decomposition of TPA ions.

- the two 1S carbon peaks located at 281.4 eV and 284.9 eV (see Table 12) may probably be attributed to TPA ions being in two different environments. However, it is most likely that the 284.9 eV peak is due to the presence of CO_3^{2-}.

It is noteworthy that surface aluminium was undetectable on all three zeolite samples. In the absence of a proper reference material, it was not possible to unequivocally identify the form of superficial iron. An iron oxide type not necessarily FeO(OH) may be present.

4.0 ACTIVATION OF METAL-CONTAINING ZEOLITES BY REDUCTION

The reduction of a metal oxide MO by hydrogen to form the metal M and water vapour may be represented by the general equation

$$MO(solid) + H_2 \rightarrow M(solid) + H_2O \quad \ldots\ldots(6)$$

Metal oxides whose standard free energy change for the reduction G° is negative (see Figure 1#) can be reduced. For a certain number of metals whose G° is positive, reduction may still proceed if the partial pressure P_{H_2O} is lowered sufficiently at high temperatures such that the term $RT\log(P_{H_2O}/P_{H_2})$ in equation (7) is rendered sufficiently negative to nullify the positive G°.

$$\Delta G = \Delta G^\circ + RT \log(P_{H_2O}/P_{H_2}) \quad \ldots\ldots\ldots(7)$$

The degree of reduction of a bulk oxide directly to the metal may be followed as a function of time for various temperatures and pressures of the reducing gas. Constituting the kinetics of the reduction, the data obtained can be interpreted mechanistically in term of the nucleation model or the contracting sphere model (90).

The metals of most interest in this project were iron, cobalt, nickel, boron and lanthanum. Under the conditions of reduction employed only Fe, Co, and Ni can be reduced to their respective metals. Boria and lanthanum oxide which have high positive G° values are not reduced.

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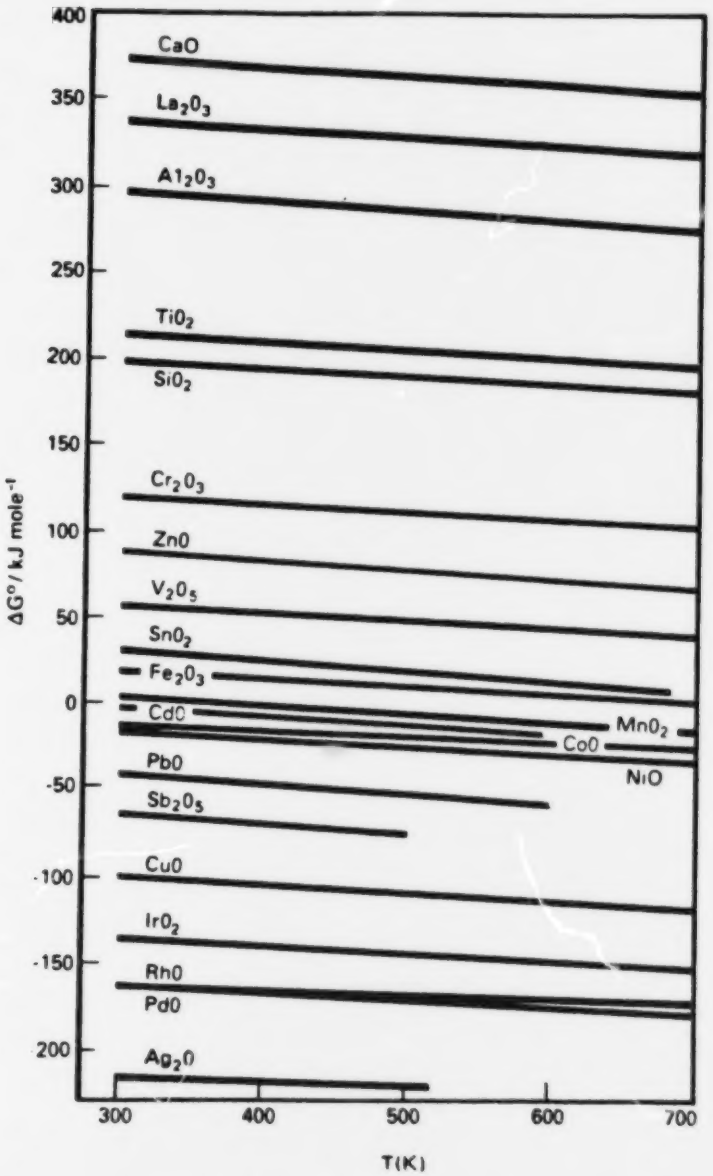

FIG. 11 Standard free energy change ($\Delta G°$) as a function of temperature for the process: Metal oxide + H_2 → metal + H_2O.

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Hydrocracking and reforming catalysts used in the petroleum industry comprise of zeolites containing reduced metals either in a dispersed state or as small clusters. ZKQ-IB zeolites do contain catalytically active metals. In the absence of a standard reduction procedure for activating such a type of catalysts, it is all the more important to have an understanding of the kinetics and mechanism of reduction. The activity of metal-containing zeolite catalysts heavily depends on the location of the metal as well as on its degree of dispersion.

When hydrogen is used to reduce a metal ion located in a zeolite, Ze, according to the stoichiometric reaction represented by equation (8), the liberated protons react with the zeolite lattice to produce hydroxyl groups, as indicated in equation (9). The "loosely bound" hydrogen of the hydroxyl group may give rise to Bronsted acidity.

$M^{n+} + n/2\ H_2$ ----- $M^{\circ} + nH^{+}$ .....(8)

$nH^{+} + nZeO^{-}$ ------$nZeO\text{-}H$.....(9)

In a review of the reduction of transition metal ions in zeolites. Uytterhoeven (91) observed a correlation between the reducibility and standard electrode potential. The higher the positive value of the standard electrode potential, the easier is the reduction. Conversely, the lower the negative value of the standard electrode potential, the more difficult is the reduction. A novel method of reducing metal ions in a zeolite involves the use of a metal ion whose standard

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electrode potential is below that of the metal ion to be reduced; for example, the reduction of nickel ions in a zeolite (s.e.p.-0.23V) can be carried out in the presence of cadmium ions (s.e.p.-0.40V) in the zeolite pore structure.

Mahoney et al (92) found that the temperature programmed reduction (TPR) of a dehydrated Fe^{2+} exchanged form of NaX zeolite gave two peaks: the more prominent one at about 703°K (430°C) and the other very weak one at about 923°K (650°C). The hydrogen consumption was found to be much less than that required for even a one-electron reduction (93). The low consumption of hydrogen was also observed by McNicol (100) in a study of the reduction of ferric oxide physically mixed with γ-Al_2O_3 and also with Pt/γ-Al_2O_3.

Unmuth et al (93) studied the reduction of Fe_2O_3-SiO_2 by TPR. The TPR profile showed two peaks at about 580 and 720°K (307°C and 447°C) which are attributed respectively to the following two reactions:

At 307°C: $H_2 + 3\ \alpha\text{-}Fe_2O_3 \longrightarrow 2\ Fe_3O_4 + H_2O$

At 447°C: $4H_2 + Fe_3O_4 \longrightarrow 3\alpha\text{-}Fe + 4\ H_2O$

TPR profiles for various metal ions in zeolite obtained by Mahoney et al are shown in Figure 12 (92).

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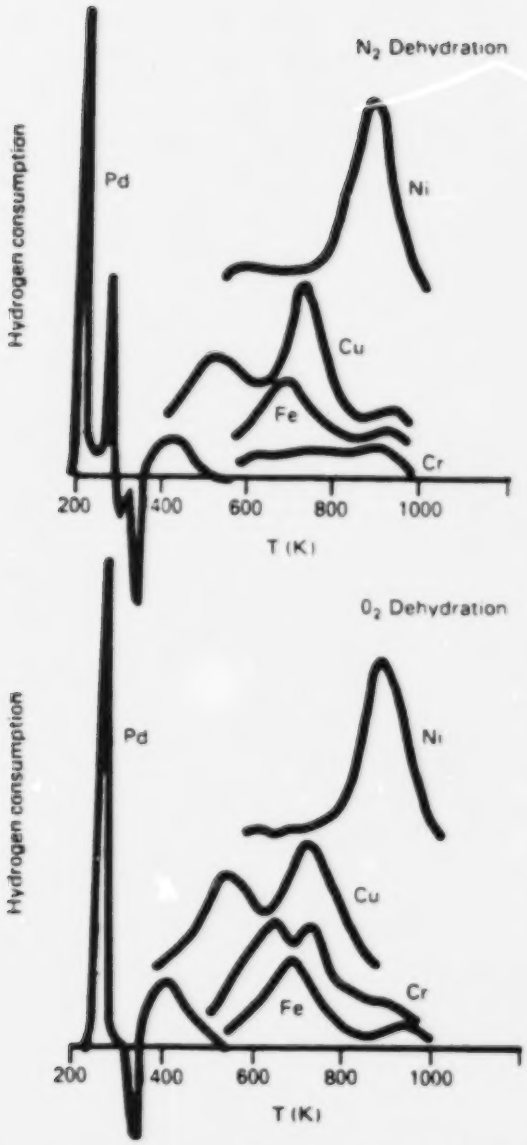

FIG.12 Tpr profiles for (M^{n+}, Na)-X-20 (M^{n+} = Pd^{2+}, Cu^{2+}, Fe^{2+}, Cr^{3+}, Ni^{2+}) after dehydration at 723 K in nitrogen or oxygen. (92)

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Anderson (94) has dealt at great length with the different ways of pretreating iron catalysts to yield the catalytically active metal itself or other interstitial compounds of iron and also with the physical and chemical changes in the catalysts during pretreatment and synthesis. On the basis of old and new data, it has been demonstrated that cementite, Hagg iron carbide, iron nitride, and iron carbonitride are at least as active in the F-T synthesis as the metal. Their activities during Fischer-Tropsch synthesis change in different ways. Generally, catalysts low in iron but containing a substantial fraction of support or carrier have been ineffective FTS catalysts. Moreover, it is difficult to prepare highly dispersed supported iron catalysts; highly dispersed iron oxide on the support cannot be reduced to the metal but poorly dispersed iron oxide can. Impregnated iron catalysts are more easily reduced in the presence of Pt or Ru (95). The impregnation of various Fe containing compounds such as carbonyl clusters on supports is one "unconventional" way to prepare highly dispersed iron particles (96, 97).

Among the usual transition metals used in the F-T synthesis, iron possesses the greatest tendency to produce elemental carbon, which may clog fixed bed reactors, and penetrate inside iron crystallites and grow to such an extent as to cause the disintegration of the catalyst particles to fines. Carbon deposition is usually not a serious problem below 275° C. At 325° C, water or hydrogen-containing molecules increases the Boudouard reaction. According to Shultz et al. (98), the carbon deposited by the action of CO or synthesis gas on various forms of iron constitutes a long-life catalyst whose activity is attributed to the crystallites of iron embedded in the carbon.

The surface concentration of iron of ZKQ-IB is rather low and it may be highly dispersed in a matrix of silica. In accordance with what has been mentioned above, this highly dispersed iron "oxide" would prove extremely difficult to reduce to the metal. The opposite would be true if the iron "oxide" was poorly dispersed; upon reduction large iron crystallites would be formed.

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In view of the rather low surface iron concentration which is most likely present as a highly dispersed entity, we have accordingly chosen only to carbide all unreduced HZKQ-IB preparations with synthesis gas having a $CO:H_2$ ratio of 1 prior to synthesis reaction proper. Future work on the pretreatment of HZKQ-IB zeolites will be centered on attempts to reduce (if feasible) surface oxides of iron by hydrogen at relatively high temperatures (450° C), followed by carbiding with synthesis gas or pure carbone monoxide at lower temperatures in order to prevent formation of elemental carbon.

It is noteworthy that finding the right method of pretreatment for ZKQ-IB zeolites is one of the most important aspects of the work aimed at developing selective catalysts which show excellent durability and easy regenerability, hence indicating practical lifetimes- for fuel production from syngas.

5.0 SYNTHESIS GAS CONVERSION TESTING OF HZKQ-IB ZEOLITES

The test programme consisted of the following tasks:

TASK 1

An attempt to determine the "optimum conditions" for the pretreatment and activation of HZKQ-IB zeolites prior to synthesis reactions. Reduction of the zeolites by hydrogen prior to carbiding was not carried out in view of the reasons mentioned in the previous section. Accordingly, only carbiding of the zeolites was effected.

TASK 2

a) Testing of each of the zeolites in regard to synthesis gas conversion to gasoline for a period of time of not less than 1 week, excluding the time taken for pretreatment of the zeolite according to the pretreatment procedures established in Task 1.

b) An attempt to determine the effect of treating the zeolite with steam at an elevated temperature on activity, selectivity, and yield of hydrocarbons.

TASK 3

a) On the basis of results obtained in Task 2, select the most promising base zeolite among those tested and modify it in an attempt to reduce CO_2 production while simultaneously favouring that of water, and to increase selectivity to liquid hydrocarbons, in particular.

b) Test each of the modified zeolites for at least 1 week, excluding the pretreatment time.

TASK 4

On the basis of the test results, select the two most promising catalysts and prepare sufficient quantities of them (200 g of each) for testing in modified Berty reactors at Queen's University.

5.1 Catalysts

Three series of ZKQ-IB catalysts were tested:

a) The A-series of catalysts consisted of IB1A, IB1A steam-treated, IB2A, IB3A and IB4A;

b) The B-series comprised only IB1B;

c) The C-series based on base zeolite IB2A consisted of Co-IB2A, Ni-IB2A, La-IB2A+(Co) and IB2A-(Co+La).

The catalysts of the A-series were prepared by changing the mole ratio of Si/(Fe+B) of the reaction mixture prior to hydrothermal crystallization. The B-series was prepared by substituting sodium tetrahydroborate for boric acid as the source of boron. The catalysts of the C-series were prepared by exchanging and/or impregnating base zeolite ZKQ-IB2A with one or more of the following elements: Ni, Co and La. Prior to the test in micro-reactors, the catalysts were pressed under 40 tons for 10 minutes into disks, which were subsequently crushed and sieved 10-20 mesh.

Eight (8) mL weighing between 2 to 3 grams of each of the catalysts were used in each test.

5.2 Testing unit

A schematic diagram of the synthesis gas conversion testing unit consisting among other things of two similar independent fixed-bed tubular reactors is shown in Figure 13. The reactor itself was a half-inch o.d. 316 stainless steel tube with a 1/16 inch o.d. inside thermowell, which allowed the positioning of three thermocouples at the top, middle and bottom of the catalyst bed. The reactor was surrounded by an aluminium block heater whose temperature was controlled to within $\pm$ 1°C. The temperature variation along the bed was found to be within $\pm$ 2°C; it can thus be said that all test runs were carried out under essentially isothermal conditions. The mass flow controllers were calibrated prior to the test.

Feed synthesis gas obtained by mixing hydrogen and carbon monoxide in the desired ratio was analysed by on-line g.c once a day. Light product gases and unconverted synthesis gas were analysed once every two hours during the test run. Liquid products on the low pressure side as well as the high-pressure side were collected once every two days. The yields of liquid hydrocarbons provided both qualitative and quantitative data on the various components contained therein. With the aid of a computer software which we have developed these and other data were used to calculate the material balance for each test run.

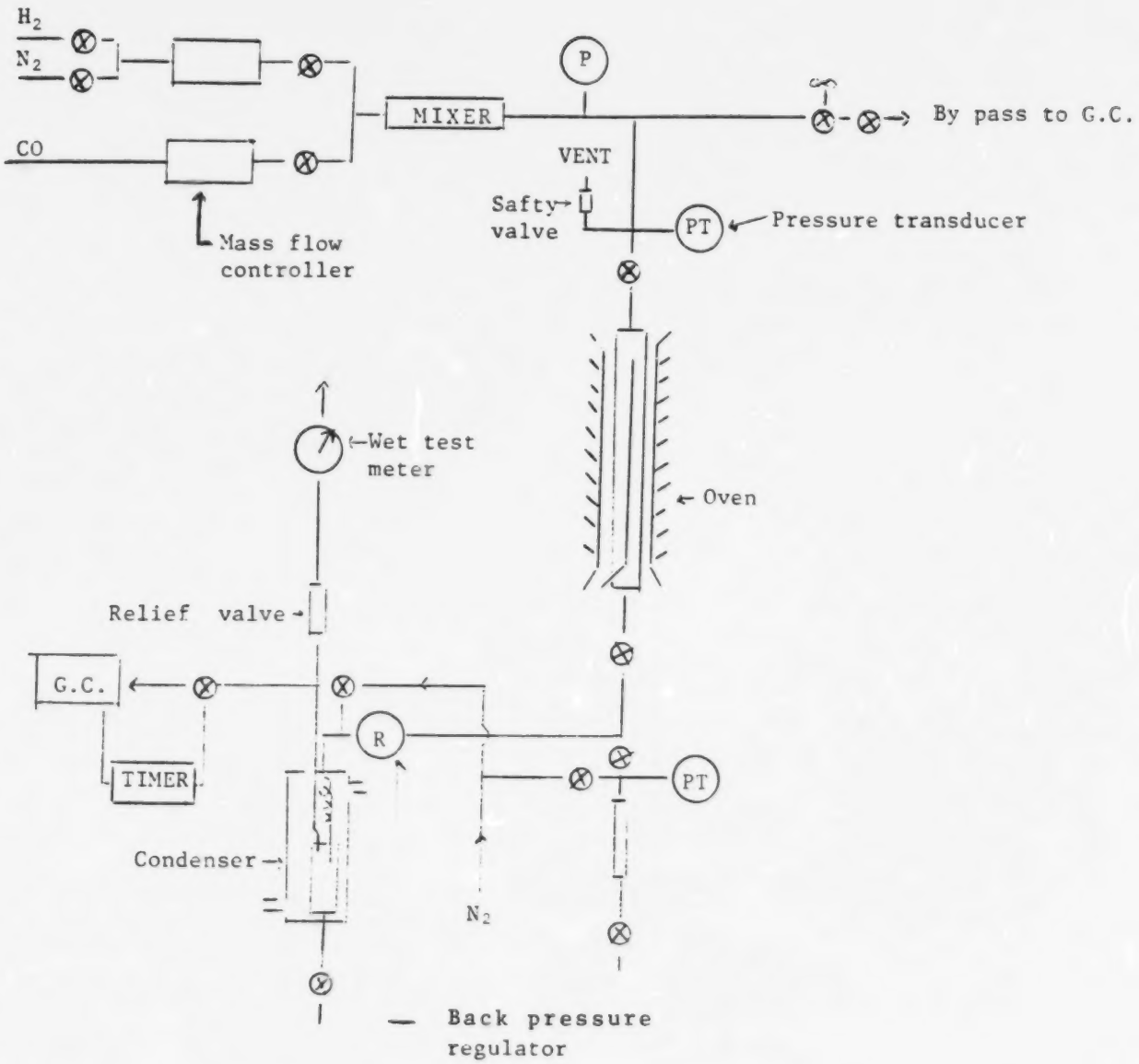

Figure 13: Schematic diagram of the micro-reactor system.

5.3 Instrumental analysis

C_1 to C_5 hydrocarbons as well as H_2, CO, CO_2, and N_2 were analysed on an on-line Hewlett-Packard gas chromatograph, model HP5790A, equipped with the following columns:

1. A 5 ft column packed with 30% DC 200 silicone oil on 80/100 mesh chromosorb PAWIB placed in series with a 24 ft column packed with 16% bis-2- methoxyethyl adipate on 80/100 mesh chromosorb PAW was used to analyse C_3 to C_5 hydrocarbons;

2. A 6 ft Porapak Q 80/100 mesh was used for the analyses of CO_2, C_2H_4 and C_2H_6;

3. A 10 ft Molecular Sieve B 45/60 mesh column was used to analyse N_2, CH_4 and CO.

Standards comprising of pure gas mixtures purchased from Matheson were used to calibrate instrument response. The composition of the liquid organic phase characterised by its PONA content (Paraffins, Olefins, Napthenes, Aromatics) was determined on a Hewlett-Packard gas chromatograph, model HP 5880, equipped with a 50 meter capillary fused silica column and a Hewlett-Packard software for PONA analysis.

The PONA calibration table supplied by Hewlett-Packard was used to verify peak positions on the chromatogram in terms of retention times. Oxygenates such as alcohols, acetone, and organic acids were analysed on a Varian 3700 gas chromatograph equipped with a chrom 220 column.

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5.4 RESULTS AND DISCUSSION REGARDING PRETREATMENT AND TESTING OF CATALYSTS

5.4.1 Pretreatment of catalysts

For reasons mentioned in the preceding section, no attempt was made to prereduce the catalysts with pure hydrogen before carbiding with synthesis gas. The catalysts were all pretreated with synthesis gas. In an attempt to find the "optimum" pretreatment conditions for the catalysts, several runs based on a typical ironborosilicate catalyst such as ZKQ-IB1A were conducted under different conditions of pressure, H_2/CO ratio, final temperature and heating rate. During pretreatment with synthesis gas, the product gases were analysed hourly by an on-line gas chromatograph. The pretreatment conditions employed for the various runs are summarized in Table 14.

5.4.2 Run 1

As seen in Table 15 which gives the results for Run 1, synthesis products such as methane and CO_2 were detected at a temperature as low as 109° C. The production of CO_2 via the Shift reaction would be most unlikely at this low temperature. As mentioned in section 2, a more likely explanation would be that the concurrent formation of methane and carbon dioxide is due to the hydrogenation of CO according to the following undesirable exothermic side reaction:

$$CO + 2\ H_2 \rightarrow CH_4 + CO_2$$

TABLE 14

SUMMARY OF THE REDUCING CONDITIONS FOR ZKQIB1A

RUN #	TEMPERATURE PROFILE °C	FINAL REDUCING		Flow rate GHSV.h^{-1}	Ratio H_2/CO	Pressure kPa
		Temp°C	Time-h			
1	109 - 355°C 1°C/min	320	22.5	600	2.11	515
2	25 - 448 25-162,5°C/min 162-448,2°C/min	448	1	600	2.43	515
3	255 - 377 1°C/min	377	18	600	2.21	515
5	260 - 400 3°C/min	375	12	600	1	515
6	250 - 450 3°C/min	380	13	600	1	75
7	250 - 450 3°C/min	380	13	600	2	75

TABLE 15

Run no 1

GAS ANALYSIS

TIME (h)	TEMP. (°C)	H_2	CO	CO_2	N_2	CH_4	C_2H_6	C_2H_2	C_3H_8	C_3H_6	n-C_4	i-C_4	i-$C_4^=$	i-$C_4^=$	c-$C_4^=$	t-$C_4^=$	$C_4^=$	n-C_5	i-C	% mole conversion CO	% mole conversion H_2
										% weight											
0	25	12,66	84,21	--	3,13	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
1	109	13,22	85,82	0,081	0,838	0,039	—	—	—	—	—	—	—	—	—	—	—	—	—	1,60	—
2	150	13,10	85,99	0,129	0,720	0,053	—	—	—	—	—	—	—	—	—	—	—	—	—	2,30	0,98
3	200	13,28	85,73	0,249	0,687	0,056	—	—	—	—	—	—	—	—	—	—	—	—	—	2,89	—
4	250	11,07	85,72	0,512	0,597	0,196	—	—	—	—	—	—	—	—	—	—	—	—	—	3,03	1,66
5	308	12,77	82,73	0,497	0,619	1,016	—	—	1,55	—	0,121	0,699	—	—	—	—	—	—	—	3,52	0,96
6	355	11,67	73,40	7,40	0,599	2,57	1,050	—	1,84	0,402	0,395	0,187	—	0,110	—	0,045	—	0,206	0,213	9,21	3,95
22,5	320	12,63	84,29	1,315	0,482	0,667	0,197	—	0,119	0,041	0,079	0,051	—	0,098	—	—	—	—	—	3,53	3,85

As expected, the molar % conversion of CO increased with increasing temperature. C_3 and C_4 hydrocarbons were detected at 308° C but they could have been formed between 250° C and 308° C. Oddly enough, no C_2 hydrocarbon was detected at 308° C. An abrupt increase in CO conversion and CO_2 formation was observed at 355° C with concomittant production of C_1 to C_5 hydrocarbons. Again as mentioned in section 2, CO_2 derived from the Shift reaction is favoured by high temperature, at which temperature some CO_2 is also formed via the Boudouard reaction.

When the temperature was lowered to 320° C and kept at that point for 22.5 hours, surprisingly no C_5 hydrocarbons could be detected. This seem to imply deposition of elemental carbon on the catalyst surface and synthesis occured concurrently. Of significance is the fact that at 355° C the rate of the Shift reaction was substantially raised; so was that of methane production. The % mole conversion of CO jumped from 3.52 to 9.21.

Run 2

In an attempt to obtain more information on the effect of temperature on catalyst pretreatment, the experiment was carried out over an extended temperature range of 162° C to 448° C by increasing the temperature in 50° C steps at a heating rate of 2° C/ minute and maintaining constant each temperature for 2 hours before raising the temperature by 50° C. The results are reported in Table 16.

Ethane and propane were easily measurable at 254° C in this run whereas in run 1 they were not detectable at 308° C. This seems to suggest that keeping the temperature constant for 2 hours at a particular value after each 50° C raise favoured the synthesis of higher hydrocarbons at lower temperatures. As expected, there was a pronounced increase in CO conversion and CO_2 formation between 254° C and 352° C. C_5 hydrocarbons were detected at 304° C. The absence of any consumption of hydrogen can only suggest that the analytical results for hydrogen are wrong. Indeed, it proved difficult to determine hydrogen at very low level of conversion. A slightly greater than 100% increase in CH_4 and CO_2 selectivities was observed when the temperature was increased from 400° C to 448° C; in that same temperature range, however, C_5 hydrocarbons were not detected, although they were easily measurable at 304°C. This is indeed surprising. The only plausible explanation is that any C_5 hydrocarbons formed were immediately cracked by the zeolite in that high temperature range.

The difference between the results of runs 1 and 2 seems to reflect the importance of allowing the temperature of the catalyst bed to stabilize to reach thermal equilibrium in a reasonable period of time before it is further increased. In order, (a) to achieve a reasonable conversion of CO during synthesis, (b) to reduce rapid build-up of elemental carbon so as to prevent premature deterioration of the catalyst, (c) to reduce sintering of the catalyst, and in view of the fact that during pretreatment at 304° C in run 2, there was simultaneous synthesis of C_1 to C_5 hydrocarbons, it was decided that the maximum pretreatment temperature should be at most 75° C above the synthesis temperature of about 300° C.

TABLE 16

Run no 2

GAS ANALYSIS

TIME (h)	TEMP. (°C)	H_2	CO	CO_2	N_2	CH_4	C_2H_6	C_2H_2	C_3H_8	C_3H_6	n-C_4	i-C_4	i-$C_4^=$	i-$C_4^=$	c-$C_4^=$	t-$C_4^=$	C_4^{2-}	n-C_5	i-C_5	% mole conversion CO	% mole conversion H_2
										% weight											
0	29	14,68	84,46	--	0,86	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
2	162	15,41	82,29	0,126	2,15	0,024	--	--	--	--	--	--	--	--	--	--	--	--	--	5,95	--
3	203	15,56	82,54	0,243	1,60	0,066	--	--	--	--	--	--	--	--	--	--	--	--	--	6,32	--
4	204	15,64	82,73	0,215	1,34	0,073	--	--	--	--	--	--	--	--	--	--	--	--	--	5,85	--
5	254	15,52	82,13	0,691	1,26	0,255	0,057	--	0,079	--	--	--	--	--	--	--	--	--	--	6,05	--
6	254	14,57	81,58	0,436	1,95	0,263	0,066	--	0,088	--	--	--	--	--	--	--	--	--	--	6,49	--
7	304	14,83	76,46	3,35	1,34	1,580	0,674	0,046	0,684	0,147	0,355	0,255	--	0,127	--	0,052	--	--	0,156	10,38	--
8	304	14,81	76,70	3,23	1,046	1,495	0,641	--	0,655	0,148	0,419	0,211	--	0,169	--	0,064	--	0,209	0,217	10,75	--
9	352	13,07	63,85	7,88	0,820	2,691	1,185	--	1,104	0,291	0,458	0,205	--	0,101	0,041	0,077	--	0,205	0,185	16,09	1,21
10	352	14,71	75,05	5,74	1,24	2,11	0,891	--	0,790	0,219	0,349	0,148	--	0,160	--	0,074	--	0,353	0,176	13,56	--
11	400	14,62	71,77	7,82	1,09	2,44	0,808	--	0,675	0,111	0,248	0,100	--	0,068	--	--	--	0,132	0,117	14,67	0,01
12	400	15,07	75,19	5,85	0,770	1,93	0,510	--	0,426	0,078	0,132	0,094	--	--	--	--	--	--	--	11,90	--
13	448	14,22	67,21	11,85	0,758	4,18	0,840	--	0,636	0,096	0,151	0,093	--	--	--	--	--	--	--	18,52	0,86
14	448	14,21	68,75	10,61	0,714	4,28	0,757	--	0,480	0,055	0,116	0,041	--	--	--	--	--	--	--	17,04	1,39

Run 3

In this run the pretreatment temperature was increased from 50° C to 250° C in about 50 minutes and then kept at that point for 40 minutes. Thereafter, the temperature was slowly raised at a rate of 1° C/minute to 377° C, which was held constant for the next 18 hours while maintaining the same flow of synthesis gas. After completing the pretreatment, the pressure was increased to 1520 kPa and the H_2:CO feed ratio was adjusted to 1.22. Synthesis gas conversion tests were conducted consecutively at 378° C and 304° C. From the results given in Table 17, the following remarks can be inferred:

- even after a pretreatment at 377° C for 18 hours, no C_5^+ hydrocarbons were detected. This is in sharp contrast to the results of run 2 which showed the presence of C_5 hydrocarbons in measurable amount in the product obtained during the run at 304° C. This difference in behaviour of the catalyst may be ascribed to the different manner in which the reactor was lined out during pretreatment;

- during synthesis at 378° C the increased in the conversion of the synthesis gas paralleled that in the formation of CO_2;

- with the synthesis temperature lowered from 378° C, there was a rapid drop in CO conversion. A gradual increase in hydrogen conversion was observed. The drop in CO conversion may be attributed to the saturation of the catalyst's surface with adsorbed OH species and carbon. Despite the drop in CO conversion, there was a gradual increase in C_1-C_5 and CO_2 selectivities. The CO_2 may at least in part have been formed via the reaction between the accumulated surface OH species with adsorbed CO or CO gas according to the equation

  $OH_{ads.} + CO_{ads.} \rightarrow CO_2 + H_{ads.}$

TABLE 17

Run no 3

GAS ANALYSIS

TIME (h)	TEMP. (°C)	H_2	CO	CO_2	N_2	CH_4	C_2H_6	C_2H_2	C_3H_8	C_3H_6	n-C_4	i-C_4	t-$C_4^=$	i-$C_4^=$	c-$C_4^=$	t-$C_4^=$	$C_4^=$	n-C_5	i-C_5	% mole conversion CO	% mole conversion H_2
										Zweight											
0	25	13,09	85,96	--	0,757	—	—	--	--	--	—	--	—	—	—	—	—	—	—	--	--
0,66	25	13,53	85,81	—	0,659	--	--	--	—	--	—	—	—	—	—	—	—	—	—	—	—
1,75	255	13,41	84,88	1,24	0,407	0,066	--	--	--	--	—	--	—	—	—	--	--	—	—	1,30	1,14
2,75	300	13,48	83,99	1,80	0,431	0,267	0,038														
3,75	325	13,51	83,71	1,65	0,427	0,499	0,120	—	—	—	—	—	—	—	—	—	—	—	—	2,38	0,68
4,75	351	12,95	82,87	2,56	0,481	0,683	0,198	—	0,069	0,025	—	—	—	—	—	—	—	—	—	2,83	0,96
23,50	377	13,07	80,62	3,30	0,695	1,03	0,317	0,065	0,141	0,053	0,062	--	—	—	—	—	—	—	—	3,30	4,18
26,75	378	6,78	76,29	10,53	0,779	2,14	0,791	0,088	0,371	0,165	0,145	0,098	—	0,091	0,048	—	—	—	—	4,68	1,97
27,75	378	6,21	73,74	12,26	0,874	2,41	0,909	0,099	1,09	0,182	0,522	0,332	—	0,09	—	0,039	--	0,131	0,191	12,4	10,40
28,75	378	5,96	71,80	13,51	0,917	2,64	1,022	0,112	1,30	0,291	0,696	0,424	—	0,158	0,045	0,068	—	0,261	0,294	11,8	14,50
29,75	303	7,39	87,04	1,88	0,863	0,686	0,222	0,053	1,42	0,292	0,807	0,461	--	0,203	0,059	0,088	—	0,364	0,355	12,3	16,30
30,75	304	7,56	88,64	1,19	0,871	0,935	0,146	0,041	0,277	0,120	0,344	0,182	--	0,139	0,049	0,078	--	0,364	0,301	4,8	7,1
31,75	304	7,40	88,05	1,58	0,953	0,688	0,199	0,043	0,139	0,087	0,154	0,094	—	0,111	--	0,050	—	0,271	0,144	3,9	5,7
32,75	304	7,24	88,32	1,41	0,863	0,713	0,208	0,043	0,188	0,102	0,171	0,111	—	0,145	0,029	0,059	—	0,194	0,127	4,3	7,5
33,75	304	7,14	87,79	1,74	0,802	0,858	0,270	0,040	0,173	0,110	0,173	0,109	—	0,172	0,041	0,065	--	0,231	0,120	2,9	8,5
34,75	304	6,96	87,30	2,03	0,889	0,962	0,316	0,044	0,209	0,127	0,200	0,125	—	0,210	0,048	0,081	--	0,155	0,124	2,2	8,5
35,75	304	6,81	86,96	2,28	0,868	1,050	0,348	0,044	0,245	0,141	0,244	0,136	—	0,248	0,056	0,092	--	0,190	0,144	1,8	10,0
36,75	304	6,70	86,63	2,53	0,847	1,120	0,378	0,047	0,274	0,145	0,270	0,139	--	0,273	0,063	0,107	--	0,219	0,153	1,35	11,2
37,75	304	6,61	86,32	2,74	0,832	1,170	0,401	0,045	0,296	0,156	0,293	0,142	--	0,299	0,067	0,106	—	0,237	0,161	0,92	11,9
38,75	304	6,47	86,08	2,96	0,808	1,230	0,426	0,050	0,319	0,161	0,311	0,145	—	0,320	0,078	0,121	—	0,296	0,170	0,61	12,5
39,75	304	6,47	85,78	3,16	0,788	1,270	0,443	0,052	0,335	0,166	0,329	0,149	—	0,334	0,081	0,128	—	0,269	0,175	0,38	13,9
	BY PASS	7,94	91,55	--	0,520	--	—	—	0,353	0,176	0,342	0,151	—	0,353	0,081	0,131	—	0,281	0,178	—	12,9
	BY PASS	7,96	91,53	--	0,511	—	--	—	--	—	--	--	—	--	--	—	--	—	--	—	--
									--	—	--	--	—	--	--	—	--	—	--	--	--
																				—	--

As is to be expected, increasing the operating pressure from 515 kPa to 1520 kPa tended to increase overall conversion of synthesis gas.

Runs 5, 6 and 7

In these runs, which were conducted to test the effect of pressure and H_2:CO ratio, each catalyst was subjected to identical heat treatment. They were heated from 250° C to 400° C or 450° C at a rate of 3° C/minute in flowing synthesis gas whose GHSV was $600h^{-1}$. The temperature was lowered to 380° C and kept at that point for 13 hours. A summary of the pretreatment conditions is given in Table 14. Thereafter, the synthesis gas conversion tests were conducted under the following conditions:

H_2:CO ratios.....1:1 (Run 5,6), 2:1 (Run 7)
Pressure, kPa.....1030
Temperatures, °C.....(i) 325 (ii) 305
GHSV, H^{-1}.....300

From the results reported in Table 18, the following remarks may be made:

- catalyst pretreated at the higher pressure of 515 kPa in run 5 gave a much lower synthesis gas conversion than the same catalyst pretreated at the lower pressure of 75 kPa in synthesis reaction at 325° C. Pretreatment at the higher pressure is apparently therefore not recommended;

- at both synthesis temperatures of 325° C and 305° C, CO conversion was higher for the catalyst pretreated

TABLE 18
H_2 AND CO CONVERSIONS, RUN 5, 6 & 7

REDUCTION:

HOURS	CONVERSION %					
	#5		#6		#7	
	H	CO	H	CO	H	CO
9	7.39	4.19	4.33	2.21	4.70	8.55
13	8.96	4.27	4.59	4.46	4.70	7.46
18	7.75	4.24	4.95	5.01	5.07	7.86

SYNTHESIS:
approximatively: 325°C

1	12.58	3.77	12.33	14.48	23.51	21.96
2	11.78	2.87	30.77	28.10	25.82	29.66
4	13.57	3.16	37.51	46.04	32.73	38.68
17	-	-	52.9	90.06	50.73	80.34

SYNTHESIS:
approximatively: 305°C

40	-	-	36.14	50.42	39.64	48.17
60	-	-	38.04	52.5	41.33	49.9
70	-	-	42.01	54.62	40.41	49.58

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with synthesis gas having a H_2:CO ratio of 1:1 (run no 6) than that for the same catalyst pretreated with synthesis gas of 2:1 ratio (run no 7). This may be the result of a better carbiding of the catalyst in run no 6 in the presence of a higher concentration of CO in the synthesis gas. It is noteworthy that CO dissociative adsorption on iron catalyst is favoured in the presence of hydrogen or any hydrogen-containing compound. Hydrogen conversions in runs nos 6 & 7 were about the same.

In light of the above, it was decided that all the prepared base zeolites would be pretreated with a 1:1 synthesis gas at a maximum temperature of 375° C for a set time of 40 hours, the heating rate being set at 2° C/minute.

5.4.3 Synthesis reaction runs

The pretreatment and synthesis conditions employed in the screening of TEN (10) catalysts are summarised in Table 19. As seen in that Table, the minimum duration of each run was 240 hours. Uncondensed products were sampled and analysed by gas chromatography once every two hours and liquid products were removed and analysed once every 48 hours over the entire duration of the run.

The results of each run are condensed in Tables 20-25, 31-34 in Appendix A. Aside from information such as synthesis conditions and weight of catalyst used, each Table gives the material balance, the product distribution in the total hydrocarbon based on carbon numbers, and the PONA (Paraffins, Olefins, Naphtenes,

Aromatics) contents of the liquid organic product, for every 48 hours on stream. Typical detailed liquid hydrocarbon distributions are shown in Appendix A.

TABLE 19

SUMMARY OF REDUCTION AND TEST CONDITIONS

CATALYST		IB1A*	IB2A	IB1A	IB3A	IB4A	IB1B	2A-Ni	2A-Co	La-2A+Co	2A-[Co+La]
TEST #		10	11	12	15	16	18	19	20	23	24
TIME-ON-STREAM		337	240	312	336	336	265	240	240	288	288
REDUCING CONDITIONS	TEMP. °C	375	375	375	375	375	375	375	375	315	315
	H_2/CO	1	1	1	1	1	1	1	1	1	1
	GHSV (h^{-1})	600	600	600	600	600	600	600	600	1000	1000
	PRESSURE kPa	101	101	101	101	101	101	101	101	101	101
TEST CONDITIONS	Temp. (°C)	310	310	310	310	310	310	310	310	310	310
	H_2/CO	0.98	0.97	0.99	1.02	1.02	0.98	1.03	1.05	1.01	0.92
	GHSV (H^{-1})	300	300	300	298	302	300	345-390	428-454	300	300
	Pressure kPa	1020-1687	1050-1276	1020	1020-1701	1020	1020	1089-1233	1316-1633	1020-1972	1020-1700

* steam activated

A list of the catalysts tested and the corresponding runs is given below.

CATALYSTS	RUNS nos.
Base zeolites-in H form	
IB-1A (steam-activated)	10
IB-1A	12
IB-2A	11
IB-3A	15
IB-4A	16
IB-1B	18
Modified IB-2A base zeolites	
Ni-IB2A	19
Co-IB2A	20
La-IB2A(Co)	23
IB-2A(Co + La)	24

5.4.3.1 Results and discussions pertaining to runs 10, 11, 12, 15 and 16

Base Zeolites:

The catalysts tested in these runs were all base zeolites. The most promising one was slated for further tests and for modification. As mentioned earlier, these base zeolites differed essentially in their respective iron contents. Their boron contents, which are partly responsible for their acidities were to all intents and purposes the same. Thus, in view of the above, we have chosen to illustrate the behaviour of HZKQ-IB2A in synthesis reaction based on run no. 11 as typical of ironborosilicate zeolites.

The analytical results of some components in the non-condensed phase are presented in Figure 14, for the first 48 hours after the start of the synthesis reaction. As seen in that Figure, CO_2 selectivity appeared to level off at around 65 wt%. During that interval there was a slow increase in CH_4 and C_2H_6 selectivities; after 48 hours they were about 6 wt% and 2.8 wt%, respectively. At 240 hours on stream, they had reached 8.8 wt% and 3.4 wt%, respectively. As shown in Figure 15, the major increase in both the CO and H_2 conversions occured during the first 100 to 120 hours and they reached 93 wt% and 82 wt% respectively after about 150 hours on stream, at which time the synthesis reaction had reached the steady state. The results show the catalyst is capable of yielding high synthesis gas conversion. In view of the very low yield of water (less than 5 wt%), see Table 22 in appendix A, the relatively high yield of oxygenate in the form of CO_2 can only be attributed mainly to the water-gas shift reaction and to a much lesser extent to the methanation of CO. For a reasonable decrease in the synthesis gas conversion, both the rates of the shift reaction and methanation can be easily reduced by a drop in the synthesis reaction temperature. At the synthesis temperature of 310° C dissociative adsorption of CO on iron catalyst does occur, leading to the formation of elemental carbon particularly in the presence of hydrogen or hydrogen containing compounds. In fact, at about 144 hours on stream there was already evidence of initial partial plugging of the catalyst bed which caused the pressure to jump from 1050 kPa to 1276 kPa. There was, however, no change in the CO and H_2 conversion. This plugging is attribu.ed to carbon deposition and

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FIG. 14 ZKQIB-2A-11-28

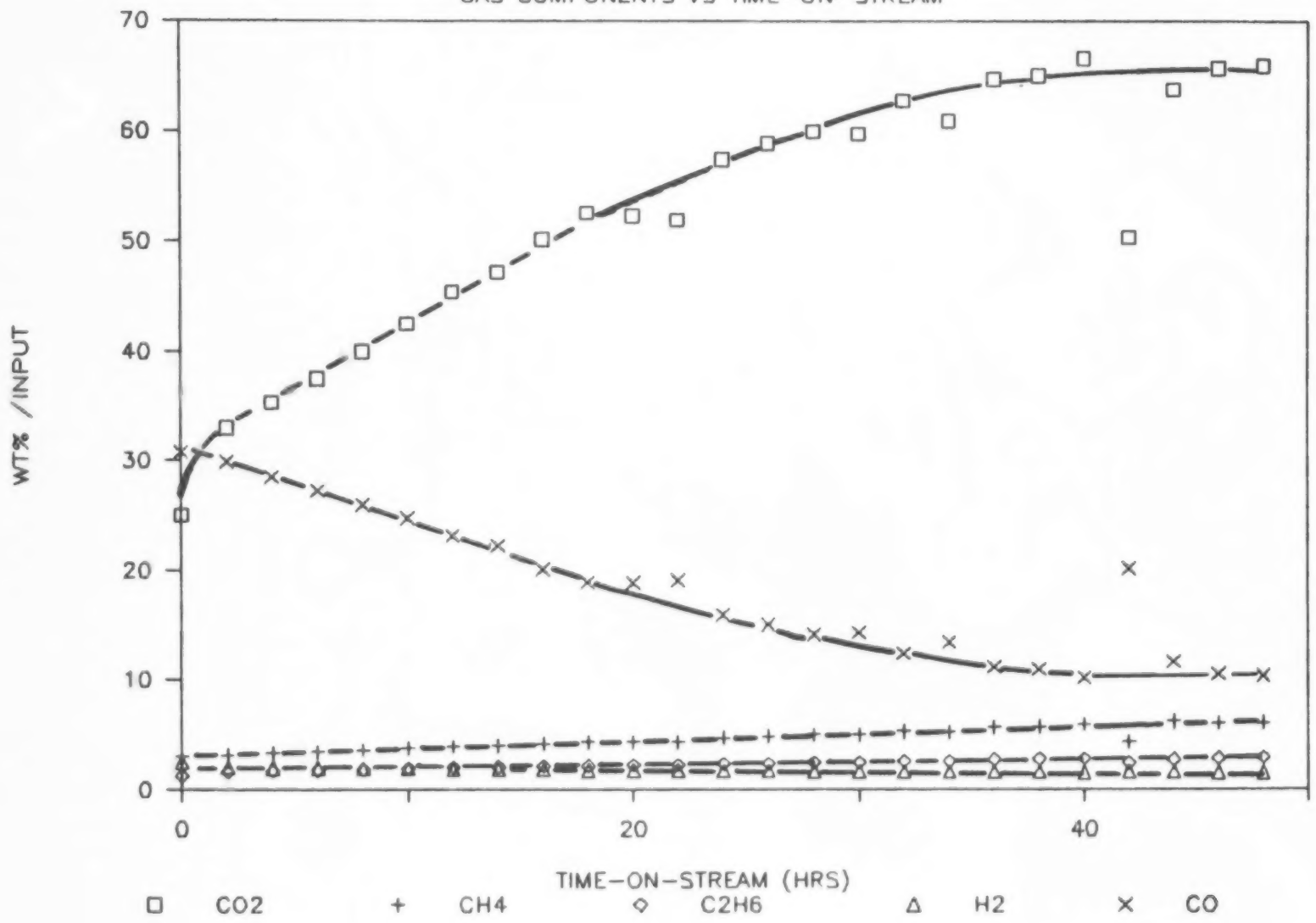
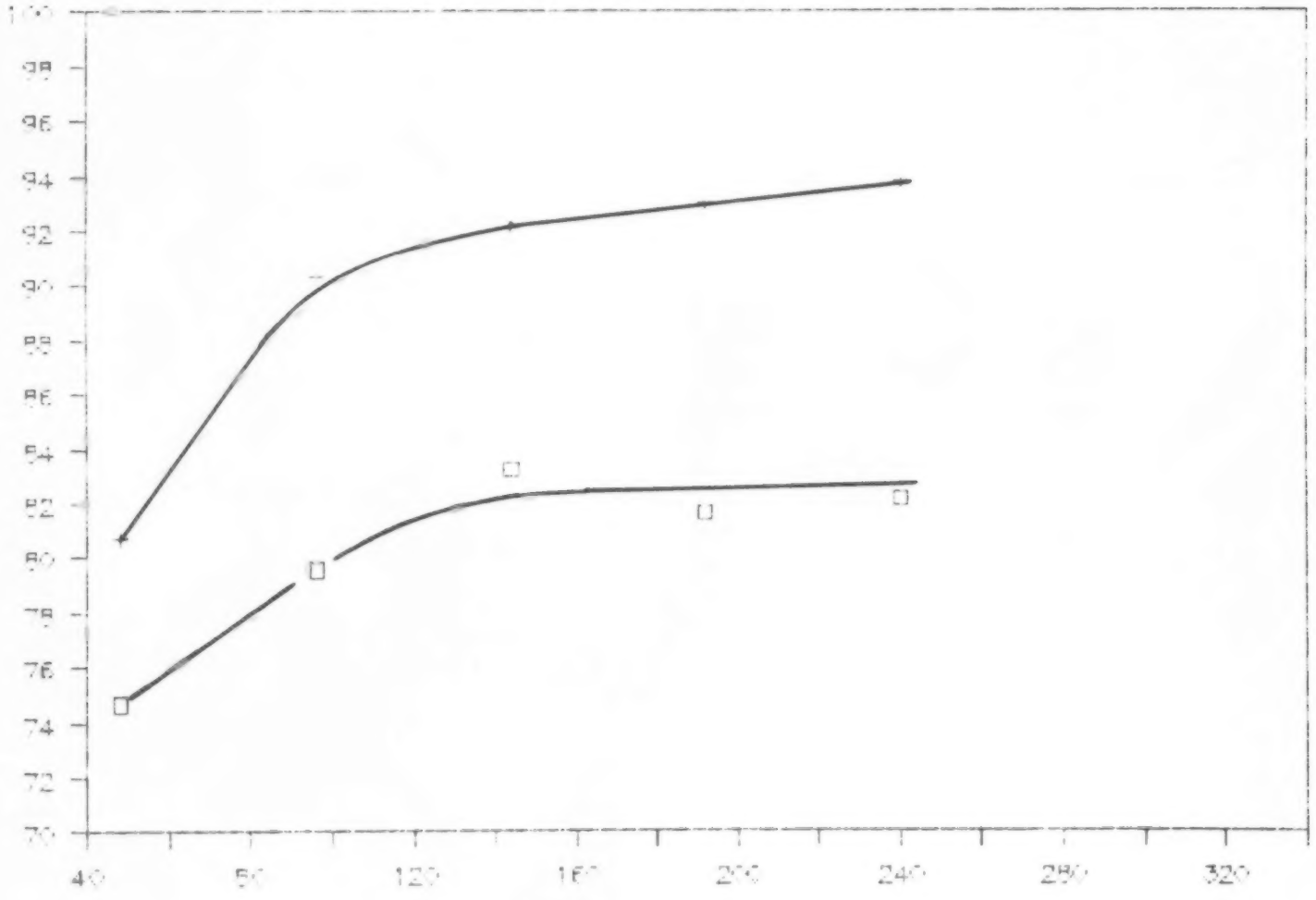


FIG. 15 CH-DIE-24-11

CONVERSION VS TIME



growth within the crystalline catalyst (27, 94).

At steady state the selectivity to total hydrocarbons was 19 wt% with respect to synthesis gas feed. This value includes the selectivity to uncondensed hydrocarbons (15.1 wt%) and that to liquid hydrocarbons (4.0 wt%). Although no significant change in both selectivities was observed after steady state was attained, as inferred from Figure 16, there was nevertheless a detectable trend towards increased selectivity to gaseous hydrocarbons accompanied by a slight decrease in C_{5+} selectivity. This trend in selectivity change with time is more clearly revealed when the selectivity to $(C_1-C_4)/C_{5+}$ is plotted as a function of time, as shown in Figure 17. As seen in that figure, the selectivity increased from about 2.2 to 3.3 over a period of time of 200 hours.

As mentioned before, water selectivity was less than 5 wt% over the entire duration of the run during which it did not show any significant variation (see Figure 18). It is quite likely that most of the water formed was converted to hydrogen and carbon dioxide by the shift reaction. At steady state, the CO_2 selectivity hovered around 65 wt%, which would seem rather high if the priority was given to saving carbon at the "expense" of hydrogen. As reported in Table 30 the results of gas chromatographic analysis of the aqueous phase demonstrate the presence of insignificant amounts of organic oxygenates.

FIG. 16 ZKQIB-2A-11

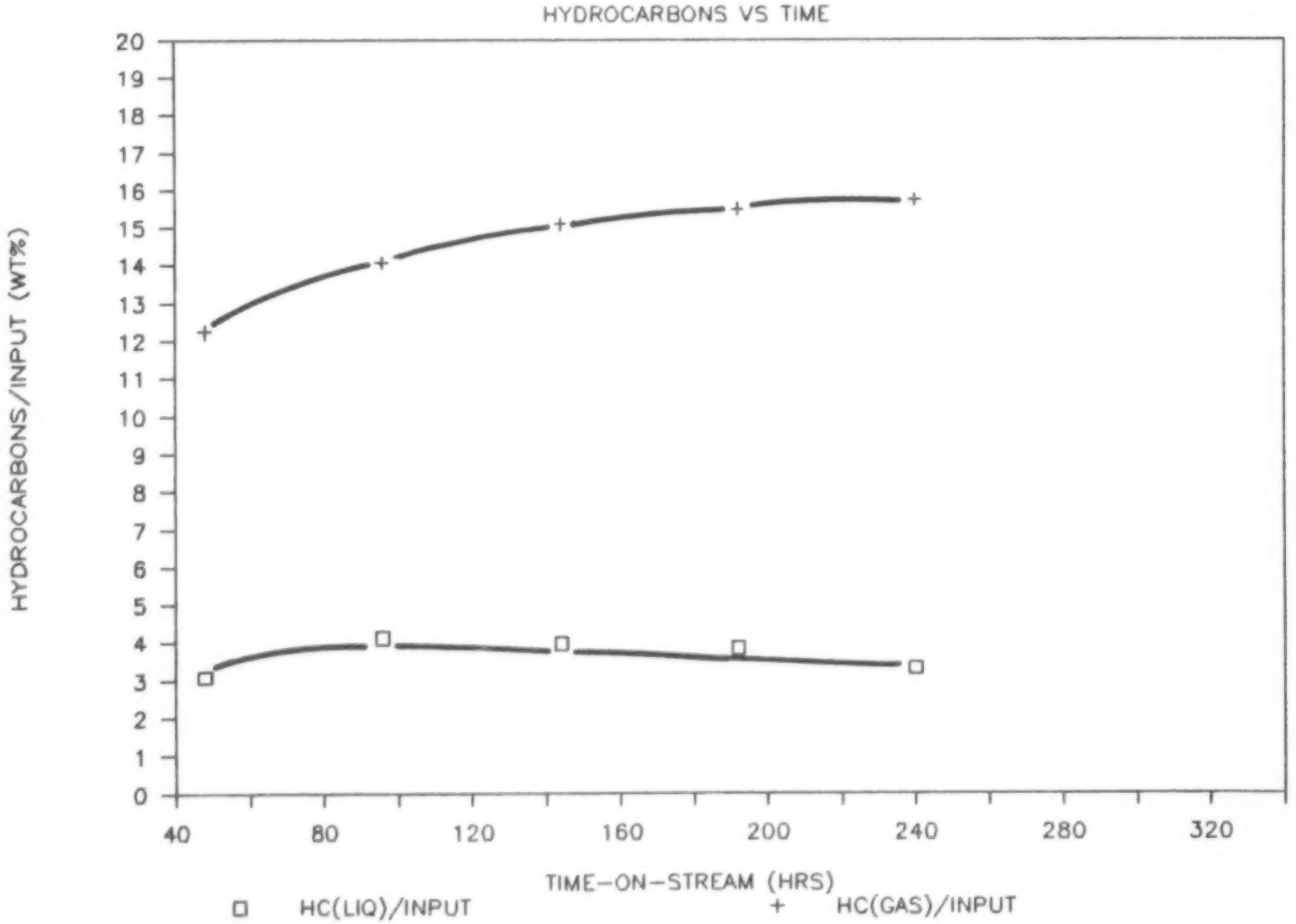


FIG. 17 ZKQIB-2A-11

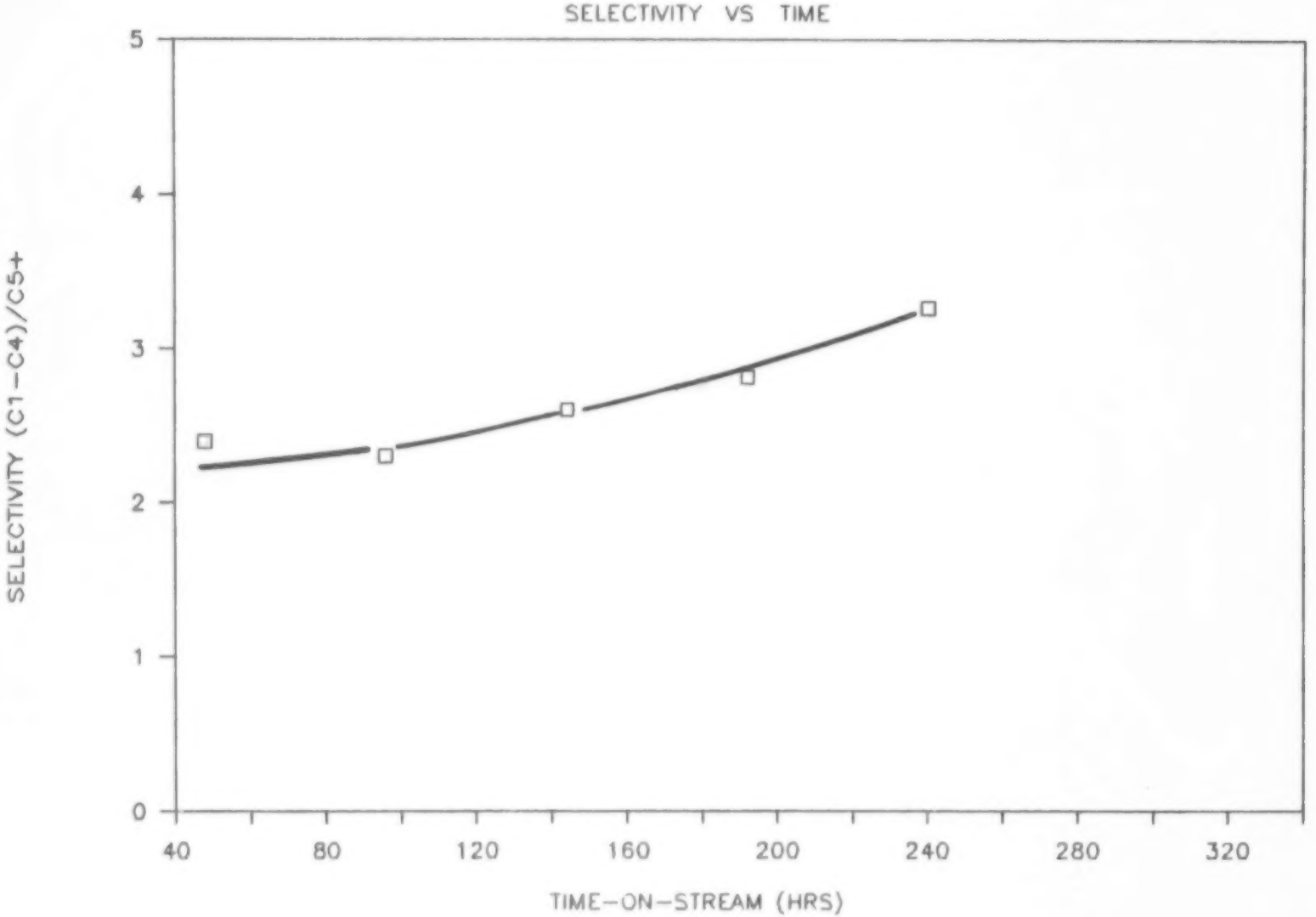
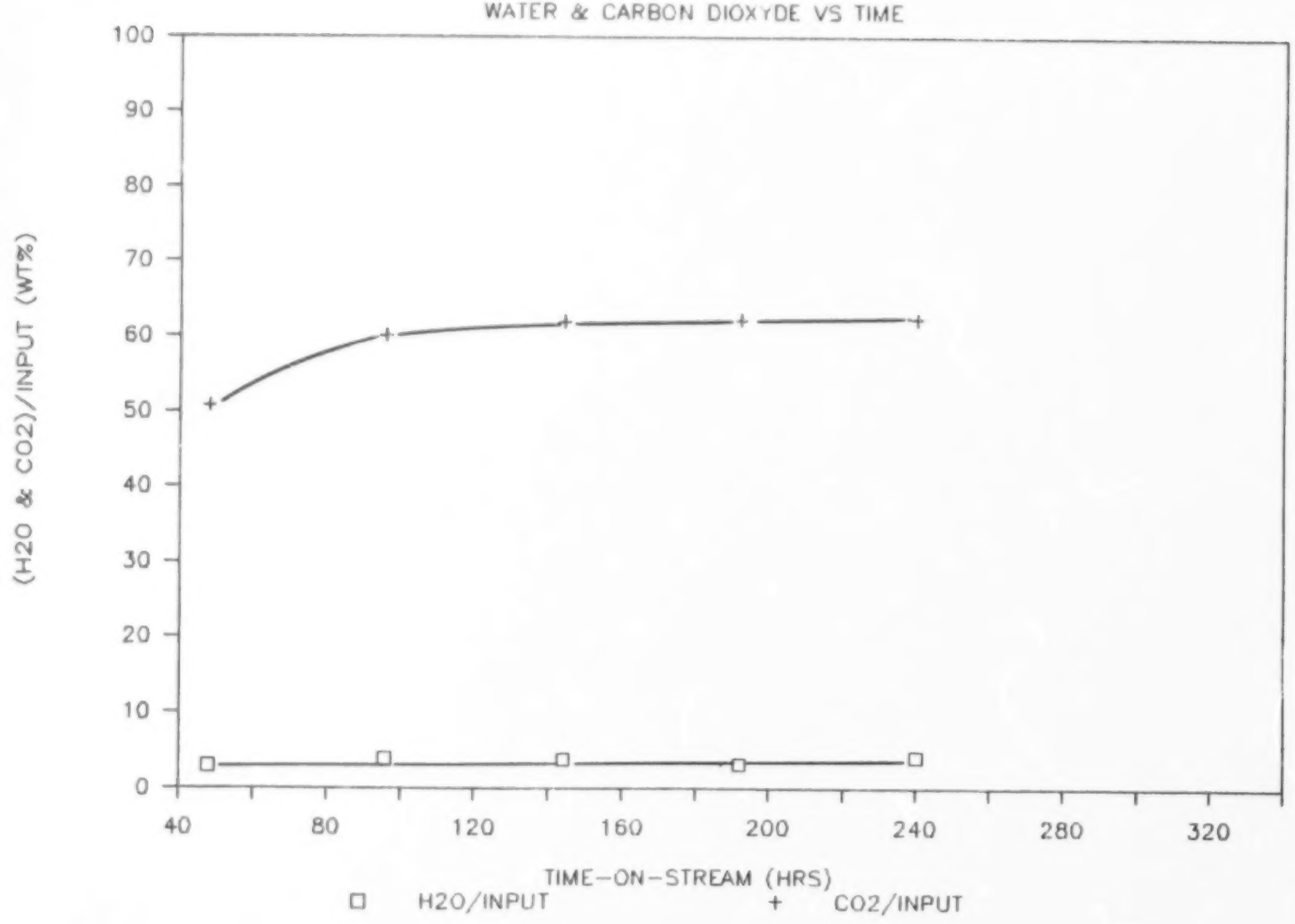


FIG. 18 ZKQIB-2A-11



The liquid hydrocarbon products were characterized on the basis of their PONA contents by capillary gas chromatography once every 48 hours over the entire duration of the run. The PONA results as a function of time which are included in Table 22 (Appendix A) are presented graphically in Figure 19. The liquid hydrocarbons produced contained about 24 wt% olefins which did not significantly vary during the run (only a slight decrease) despite the increase in pressure due to catalyst bed plugging. In like manner, the naphtenes content in the liquid product remained almost constant at about 12 wt%. Only the content in aromatics registered an increase from 32 wt% to 39 wt% over a period of 200 hours. This increase is, however, contrary to earlier observations according to which aromatics selectivity tends to decrease whereas that for olefins tends to increase as the catalyst ages. Hence, this increase in aromatics selectivity can only be due to the increase in the operating pressure from 1050 kPa to 1276 kPa. Indeed, increased pressure is believed to effect a better coupling of the olefination-aromatisation sequence of reactions on ZSM-5 type catalysts (99).

As expected the increase in aromatics selectivity was accompanied by a gradual drop in paraffins selectivity over the same time interval from 32.4 wt% to 26.9 wt%. Chang et al (99) also found that any increase in aromatics selectivity is usually accompanied by a decrease in paraffins selectivity.

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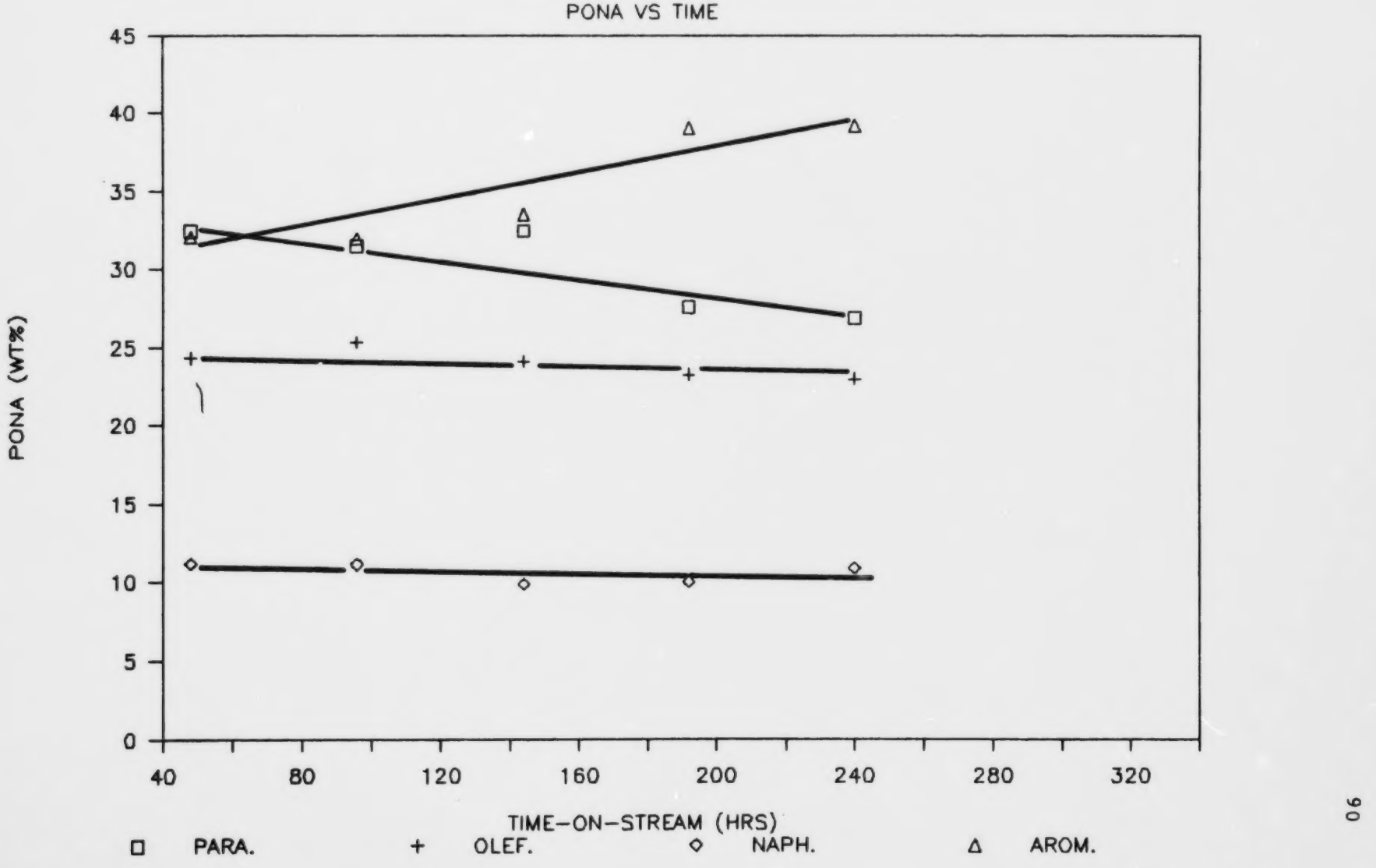
FIG. 19 ZKQIB-2A-11



An examination of the gas chromatogram of a sample of liquid hydrocarbons taken after 192 hours on stream and shown in Appendix B reveals that the product spectrum lies exclusively below C_{12}, thereby indicating that ZKQ-IB2A is highly selective to gasoline range products in synthesis gas conversion reactions. The highly olefinic nature of the gasoline is largely responsible for its high gum content and the unaceptable high cloud point of the raw gasoline as reported in Table 38. This difficulty in meeting specifications can be obviated either by mild hydrogenation of the raw gasoline and/or by treatment with antioxidants and metal deactivators.

The results of runs 10 (IB-1A steam-activated), 12 (IB-1A), 15 (IB-3A), 16 (IB-4A), and 18 (IB1B) are compiled in Tables 20, 21, 23 and 25, respectively. Although similar results to those of run 11 (IB-2A) were observed in all of these runs, there were nevertheless certain differences, both qualitative and quantitative, that warrant the following comments:

- as expected, highly olefinic gasolines were produced in all runs. On the whole, the gasolines contained slightly more olefins than that produced in run 11.

- CO conversions in runs 10, 11 and 12 were practically the same but they were definitely higher than those of runs 15 and 16. It is unlikely that the lower valve of $SiO_2/(Fe_2O_3+B_2O_3)$ ratios of IB-3A and IB-4A are attributable for the much lower CO conversion. A more likely factor would be the much lower degree of crystallinity of both these catalysts.

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- both IB-3A and IB-4A were found to have significantly lower selectivities to hydrocarbons than IB-1A and IB-2A even though their respective iron contents were higher. It is most likely that this is directly related to their much lower degree of crystallinity as reported earlier in the section dealing with characterization of ironborosilicate zeolites. Indeed, past experience with the conversion of methanol to gasoline over ZMQ-TB zeolite has shown that selectivity to hydrocarbons is influenced by the degree of relative crystallinity of the zeolite. The higher the degree of crystallinity, the better the selectivity to hydrocarbons.

- although IB-3A and IB-4A had almost identical $SiO_2/(Fe_2O_3+B_2O_3)$ ratios, the qualities of the liquid hydrocarbons produced were different in many respects. First, the liquid hydrocarbons produced over IB-4A contained the highest paraffin content (ca 56 wt%) and the least amount of aromatics (less than 9 wt%) and of naphtenes (ca 8 wt%). Secondly, the same liquid hydrocarbon product contained a certain amount of distillate with carbon number of up to C_{24}. In contrast, all the liquid hydrocarbons produced over IB-1A, IB-2A and IB-3A were in the gasoline range and contained between 28 wt% and 34 wt% aromatics. The fact that the liquid hydrocarbons produced over IB-4A were highly paraffinic and very poor in aromatics appears to be directly related to its high residual sodium content, hence to its acidity. The presence of high alkali metal content in conventional F-T iron catalyst is known to shift the product distribution to higher molecular weight range.

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Steam-activation of zeolites particularly those of the Y family have long been practised with the object of producing thermally "ultra-stable" zeolites for use in cracking operations in the petrochemical industry. Compared to aluminosilicate zeolites, which can withstand high temperatures in excess of 700° C without suffering structural collapse, borosilicate zeolites begin to show structural collapse at temperatures in excess of 650° C. With the above in mind, it was decided to test the effect of steam-activation on ZKQ-IB1A in relation with its activity and selectivity in synthesis gas conversion reaction. Accordingly, IB-1A was steam-treated at 450° C for 5 hours at atmospheric pressure prior to pretreatment with synthesis gas. The results of synthesis gas conversion run no. 10 reported for IB-1A (steam-activated) in Table 20 are compared to those of run no. 12 for untreated IB-1A in Table 21. Some of the main findings are listed below:

- CO conversion for the steam-activated zeolite was higher than that for the untreated zeolite. H_2 conversion was about the same for both zeolites;

- although the selectivity of the steam-activated zeolite to total hydrocarbons was slightly higher than that of the untreated zeolite, the latter had a higher selectivity to C_{5+} hydrocarbons; more uncondensed hydrocarbons were produced on the steam-activated zeolite. The fact that the pressure increased from 1020 kPa to 1687 kPa most probably as a result of gradual catalyst bed plugging appears to suggest that dissociative adsorption of CO on the steam-activated zeolite occurs much more readily than on the untreated zeolite. This is supported by the higher amount of product CO_2 formed on the steam-treated zeolite.

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- all things being equal, the rate of the shift reaction on both zeolites should be about the same. The different amount of CO_2 produced over both zeolites is most likely due to the higher rate of the Boudouard reaction on the steam-activated zeolite.

- the gasoline produced on steam-activated zeolite was more paraffinic and less aromatic in nature than that produced on the untreated zeolite.

In light of the results obtained for the steam-activated zeolite, it appears that this catalyst is very active and in order to reduce the incidence of reactor plugging and the formation of CO_2, the synthesis temperature should be reduced to below 300° C. It is to be noted that at the conclusion of both runs the two catalysts were still very active. One major conclusion which may therefore be drawn, concerns the iron content of the catalyst: the activity of steam-activated IB-1A is about the same as that of IB-2A in spite of the fact that it contains 8.84 wt% Fe_2O_3 as compared to 11.50 wt% Fe_2O_3 for IB-2A. It is believed that the same activity could still be achieved with a zeolite with a still lower iron content, wherein the iron is extremely "well-dispersed" either atomically or in clusters. IB-3A and IB-4A which had higher iron contents (15.3 and 15.2 wt% Fe_2O_3 respectively) than IB-2A were found to be less active than the latter. Actually, high iron content may

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broaden product selectivity instead of narrowing it, especially in situations where the primary products formed on the iron cannot all be intercepted by the zeolite component.

Futhermore, since low degree of crystallinity has been singled out as the major contributing factor to low hydrocarbon selectivity rather than the iron contents of the catalysts (within the concentration range covered by them), there remains yet another factor which seems to have a direct bearing on the selectivity to hydrocarbons. This factor is the residual sodium concentration in the zeolite. In addition, as we shall see below, it also influences both the olefinicity and isomericity of the zeolite catalysts. Residual sodium neutralises acid sites in zeolites to a degree which is dependent on its concentration.

To demonstrate the influence of residual sodium on hydrocarbon selectivity, 3 zeolites whose SiO_2/B_2O_3 ratios do not differ too much from each other, so that acidities provided by the tetrahedrally coordinated boron are essentially equivalent, were chosen and compared for their selectivities to hydrocarbons as reported in Table 26.

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TABLE 26

INFLUENCE OF RESIDUAL SODIUM ON HYDROCARBON SELECTIVITY

CATALYSTS	SiO_2/B_2O_3 (molar)	Na (p.p.m)	SELECTIVITY WT%
IB-2A	345	742	19.04
IB-3A	299	2226	15.05
IB-4A	303	5342	12.91

As seen in Table 26, there appears to be a direct correlation between degree of acidity and total hydrocarbon selectivity. As a general rule, the higher the acidity the higher the hydrocarbon selectivity.

5.4.3.2 Olefinicity and "isomericity" of ZKQ-IB zeolites in syngas conversion

Defined as the ratio of olefins/total hydrocarbons of the same carbon number, the olefinicity of each of the various zeolites was determined with respect to C_2 to C_4 hydrocarbons only. As regards the isomericity of the zeolite which is defined as the ratio of iso-compound/total hydrocarbons of the same carbon number, it was determined with respect to C_4 hydrocarbons only. In computing the results reported in Table 27, the insignificant amounts of the hydrocarbons of interest present in the liquid organic phase were ignored.

On the basis of the results obtained, the following main observations can be made:

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TABLE 27

OLEFINICITY AND ISOMERICITY OF HZKQ-IB ZEOLITES
AS A FUNCTION OF TIME ON STREAM

TIME ON STREAM (h)	$C_2^=/TOT.C_2$	$C_3^=/TOT.C_3$	$C_4^=/TOT.C_4$	iso-C_4/TOT.C_4
Catalyst: HZKQ-IB1A (Steam activated); run 10				
48	5.41	20.13	38.46	29.32
96	2.03	13.94	30.57	30.19
126	1.51	12.44	29.20	29.60
192	1.94	12.39	30.50	28.50
240	1.45	11.52	32.17	27.83
Catalyst: HZKQ-IB1A; run 12				
48	6.80	22.20	53.10	30.80
96	3.50	16.23	43.40	25.00
144	2.60	14.70	40.20	25.40
192	2.40	14.10	39.90	24.40
240	2.00	13.70	39.80	23.40
Catalyst: HZKQ-IB2A; run 11			Na: 942 ppm	
50	5.19	12.60	26.90	37.60
96	2.46	8.42	23.20	26.60
144	2.05	9.05	24.00	35.64
192	1.73	10.39	25.00	34.77
240	1.71	10.57	25.91	34.01
Catalyst: HZKQ-IB3A; run 15			Na: 2226 ppm	
46	5.46	19.41	38.96	29.87
94	3.92	18.52	41.74	26.03
142	5.38	19.05	46.38	22.55
190	5.40	19.50	47.30	21.40
238	5.50	19.80	49.50	20.30
Catalyst: HZKQ-IB4A; run 16			Na: 5342 ppm	
46	19.25	56.42	81.22	2.45
94	20.69	64.06	81.48	1.65
142	19.90	64.32	80.80	1.20
190	16.83	61.42	78.66	1.20
238	17.41	63.02	79.52	1.20

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- IB-2A displayed the lowest olefinicity and the highest isomericity while IB-4A had the highest olefinicity and the lowest isomericity. This difference in behaviour can be explained in terms of their different levels of acidity. The results presented in Table 27 illustrate the effect of residual sodium on their olefinicity and isomericity. Although the same base zeolite should have been used, it can none the less be said that, as a general rule, the higher the residual sodium content in the zeolite e.g IB-4A, the higher the olefinicity and the lower the isomericity and vice versa. The practical importance of this finding lies in the fact that by controlling the concentration of alkali metals such as sodium in the zeolite it is possible to control both its olefinicity and isomericity in order to obtain the desired product slate. Low residual sodium content would give a product rich in iso-paraffins which normally have high octane number. The presence of such constituents in gasoline and jet fuel in particular is highly desirable. On the other hand, the formation of products rich in olefins and poor in iso-paraffins and aromatics is favoured by the presence of "high" concentrations of sodium in the zeolite. These products would constitute a poor quality gasoline. It is, however, possible to control the iron and sodium contents of ZKQ-IB zeolite in such a way as to produce predominantly either light olefins which are the backbones of the petrochemical industry or higher olefins and iso-olefins in the distillate range from which diesel and/or jet fuel blending stock can be produced by mild hydrogenation. And as we shall see below the presence of yet other exchanged

and/or impregnated metals on the base zeolite does exert a major influence not only on % conversion of syngas but also on the product distribution and on the quality of the gasoline produced;

- the olefinicity of IB-1A appears to decrease somewhat while its isomericity appears to increase after undergoing steam-activation at 450° C for 5 hours at 101 kPa. It is probably unlikely that certain rearrangement which may have been brought about by steam-activation in regard to the position of boron and iron in the lattice without however changing the overall crystalline structure of the zeolite, could have been the cause of the change in olefinicity and isomericity of the zeolite. The most probable cause would be the leaching out of part of the residual sodium in the zeolite during steam activation thereby resulting in an increase in acidity of the zeolite;

- as expected, the olefinicities and isomericities of IB-1A and IB-3A were between those of IB-2A and IB-4A in view of fact that their residual sodium contents were between those of IB-2A and IB-4A.

5.4.3.3 Aromaticity of ZKQ-IB zeolites

The aromatization of light olefins over pentasil-type zeolites is best effected when the zeolites are in the acid form. The presence of residual sodium in the zeolite will accordingly be expected to result in a reduction in its aromatization power. Table 28 compares the wt% aromatics in samples of liquid hydrocarbons collected after 240 hours on stream during different runs.

TABLE 28

AROMATIZATION AS A FUNCTION OF SODIUM CONTENT

CATALYSTS	RESIDUAL SODIUM CONTENT (ppm)	WT % AROMATICS IN LHC
IB-2A	742	39.05
IB-3A	2226	31.45
IB-4A	5342	9.62

As expected, the aromatization power is drastically reduced in the presence of high concentration of residual sodium in the zeolite as a result of a decrease in its acid function which is necessary for aromatization of the olefin intermediates. Thus, in order to maximize production of aromatics and iso-paraffins it is essential that the sodium level in the catalyst be reduced to a minimum.

5.4.3.4 Coking of catalysts

The increase in operating pressure observed during some of the runs has been attributed to the gradual and partial plugging of the catalyst bed resulting from carbon deposition. As mentioned in one of the earlier sections severe coking particularly within the catalyst particles may lead to their partial or complete disintegration into fines, thereby leading to partial or complete plugging of the reactor bed or to channeling effects.

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Visual examination of the used catalysts revealed significant carbon deposit on all of them. They were all analysed for their respective total carbon contents, using the Leco furnace equipped with infrared CO_2 detector. The results are reported in Table 29, which also compares the degrees of coking of the various catalysts.

TABLE 29

CATALYSTS	RUN NO.	WT % C	GRAM OF C/100g SYNGAS
IB-1A (steam activated)	10	15.0	0.14
IB-1A	12	8.6	0.10
IB-2A	11	14.5	0.20
IB-3A	15	12.1	0.12
IB-4A	16	11.7	0.13

As seen in Table 29, IB-2A has the highest coking susceptibility. This may in part be attributed to its residual sodium content which was in fact the lowest among the various catalysts. Being more acidic than the other zeolites, IB-2A would be expected to promote more cracking thereby leading to more coke formation.

Of particular practical importance is the fact that all of the base zeolites were found to be still active at the conclusion of the runs even in the presence of the relatively high amounts of carbon, as reported above. In agreement with other findings (81), this may be explained by the shape-selective

properties of the zeolite which restrict the formation of coke within the its channels and only to its surface. It is most likely that the bulk of the carbon deposit is filamentous or vermicular carbon, which does not seem to inactivate the catalyst. Operating the reactor at higher pressures would decrease carbon deposition.

5.4.3.5 Aqueous phase

A typical graphic presentation of the yields of product water as a function of time is shown in Figure 18. The rather low and constant yield of product water was observed in all of the runs. IB-2A displayed the lowest water selectivity of about 4 wt% with respect to total syngas feed, while IB-4A had the highest at about 7 wt%. The results of gas chromatographic analyses of the aqueous phase from each run reported in Table 30 show the presence of oxygenates in insignificant amounts. This seems to imply that any oxygenates which might have been formed in significant amounts were mostly converted to hydrocarbons by the zeolite components.

5.4.3.6 Selection of base zeolite for longer duration tests and modification

From among the five base catalysts that were tested in synthesis gas conversion, ZKQ-IB2A was selected for longer duration tests in CSTR reactors of 200 mL capacity and for chemical modification in an attempt to increase liquid hydrocarbon selectivity, yields and quality of gasoline produced while at the same time decreasing CO_2 selectivity and increasing water

TABLE 30

ANALYSES OF AQUEOUS PHASE SAMPLED AT 240 HOURS ON STREAM

CATALYSTS Run No	IB-1A 10	IB-1A 12	IB-2A 11	IB-3A 15	IB-4A 16	Ni-IB2A 19	Co-IB2A 20	La-IB2A+Co 23	IB2A(Co+La) 24
Oxygenates, wt%									
Methanol	-	-	-	1.4	0.01	-	-	-	-
Ethanol	-	-	-	0.13	-	-	-	-	-
Acetone	0.36	0.42	0.05	0.076	0.043	0.09	0.64	0.02	0.2
1-propanol	-	-	-	0.046	-	-	-	-	0.012
iso-butanol	-	-	-	-	-	-	-	0.005	0.015
MEK	0.006	-	0.004	0.007	0.005	-	-	0.003	-
n-pentanol	-	-	-	-	-	-	-	0.006	0.009
2-pentanol	-	-	-	-	-	-	-	-	0.002
3-methylC_4-one	-	-	-	-	-	-	-	-	0.002

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selectivity. This selection was made on the basis of the following criteria:

- although steam-activated ZKQ-IB1A displayed a slightly higher total hydrocarbon selectivity than ZKQ-IB2A, the overall C_2-C_4/C_{5+} selectivity of the latter was consistently less than that of the former. As reported earlier, total hydrocrabon selectivities to IB-3A and IB-4A were significantly lower than IB-2A's and IB-1A's.

- the isomericity and aromaticity of IB-2A were found to be the highest while its olefinicity was found to be the lowest; such highly desirable properties are conducive to for the production of a good quality gasoline with low gum formation potential.

- no hydrocarbons beyond C_{12} were detected in the liquid hydrocarbons produced over IB-2A. Thus, its selectivity towards gasoline is very high; in contrast IB-4A co-produced gasoline and distillate which is not, however, the objective of this project.

- IB-2A had the highest relative degree of crystallinity and acidity level which are highly desirable for maximising hydrocarbon selectivity, for good thermal stability and for high aromatization and isomerisation capabilities.

5.4.4 Modification of IB-2A base zeolite by exchange and/or impregnation with metal(s) and testing thereof

The results of the previous test runs on the five unmodified ZKQ-IB catalysts have consistently shown that

a major portion of CO is lost as CO_2 during synthesis reaction mainly by the internal shift reaction. For syngas rich in CO the need to adjust the H_2/CO ratio to the proper value either by adding pure hydrogen obtained by electrolysis of water or by converting part of the CO over a dedicated external shift reactor would probably not arise if ZKQ-IB zeolite were used since it already possesses inherent powerful shift function.

Thus, this shift function can be advantageously exploited in situations where the synthesis gas is too rich in CO. The use of an external shift reactor could therefore be obviated thereby cutting capital outlay and production costs. In the majority of cases synthesis gas that is being produced nowadays prior to ratio adjustment is rich in CO. In countries where hydropower is inexpensive such that H_2 can be "inexpensively" produced via water electrolysis, the conservation of carbon at the expense of H_2 may make sense. But given the high cost of H_2 in most other situations or in industrialised regions of the world, the rejection of carbon as CO_2 via the shift reaction for the production of H_2 is the current practice.

Indeed, from the economic standpoint it would appear logical, if practically feasible, to remove carbon and conserve hydrogen whether it be in synthesis reaction or in upgrading of hydrocarbons poor in H_2 but rich in carbon, instead of literally "pumping" hydrogen into these materials to decrease the C/H ratios.

In situations where electrolytic hydrogen is readily and inexpensively available (surplus electricity being

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stored in the form of H_2) its use in adjusting the H_2/CO ratio to the required value is being proposed since this practice has the added advantage of maximising the use of co-produced electrolytic oxygen in gasification. In any event, the reasons which have prompted us to modify the base zeolite ZKQ-IB2A by ion exchange with Co, Ni, and La and/or by impregnation with Co and La were based at the outset on two major scientific observations which suited two objectives of the project.

The first objective was to attempt to reduce CO_2 selectivity by partially suppressing the internal shift function of the base zeolite by ion-exchange with Ni or Co or by impregnation with Co. Rao et al (58) had earlier reported that the addition of small amounts of cobalt to a Fe/ZSM-5 synthesis gas conversion catalyst was found to suppress the internal shift reaction that is mainly responsible for the formation of product CO_2.

The second objective was to maximize hydrocarbon selectivity either by exchanging the base zeolite with La and impregnating the exchanged zeolite with Co to suppress internal shift reaction or by impregnating the base zeolite with Co and La by the wet incipient technique.

La was selected on the basis of the fact that it would not only improve the thermal stability of the catalyst in the presence of steam but it would also confer increased Bronsted acidity to the zeolite in accordance with the following equations:

$$La^{3+} + H_2O \rightarrow LaOH^{2+} + H^+$$
$$LaOH^{2+} + H_2O \rightarrow La(OH)_2{}^{2+} + H^+$$

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The increased thermal stability confered upon the La-exchanged zeolite is attributed to the presence of sites in the zeolite framework occupied by the lanthanum-hydroxy ions. Ultra-stable rare earth forms of X and Y zeolites are commercially available while rare-earth exchanged ZSM-5 type zeolites are still a laboratory curiosity. The attempt to increase the Bronsted acidity of ZKQ-IB zeolite by exchanging it with La stems from the fact that borosilicate pentasil zeolites do not, in general, possess high intrinsic acidity.

Indeed, all things being equal, the intrinsic acidity of ZSM-5 is much greater than that of borosilicate zeolites of the ZSM-5 type. Consequently, the olefinicity of borosilicate zeolites should be greater than that of ZSM-5. This has indeed been borne out in practice. Moreover, their susceptibility to coking is less than that of ZSM-5 which effectively leads to longer cycle lengths between catalyst regeneration, hence possibly to longer useful catalyst life.

(Co + La) ZKQ-IB catalysts were therefore expected to display increased hydrocarbons and aromatics selectivity on the one hand, and on the other, decreased shift function which would be reflected in decreased CO_2 selectivity and increased water selectivity.

The procedures employed in preparing the four (4) modified IB-2A base zeolites by metal ion-exchange and/or impregnation by the wet incipient method have been described in sufficient details in an earlier section dealing with the synthesis and characterization of ironborosilicate zeolites. The four modified IB-2A

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catalysts were:

(1) Co-IB2A: Cobalt-exchanged IB-2A base zeolite
(2) Ni-IB2A: Nickel-exchanged IB-2A base zeolite
(3) La-IB2A + (Co): Lanthanum-exchanged IB-2A base zeolite impregnated with 3 wt% of cobalt
(4) IB-2A (Co + La): IB-2A in the hydrogen form impregnated with 7 wt% and 3 wt% of lanthanum and cobalt, respectively.

The four catalysts were pretreated and tested under conditions summarized in Table 19. As in the case of the base zeolites, the uncondensed phase was analysed by g.c. once every 2 hours and the liquid product was removed and subsequently analysed once every 48 hours. The results of runs 19, 20, 23 and 24 are summarized in Tables 31, 32, 33 and 34 respectively (Appendix A).

5.4.4.1 Results and discussions in regard to runs nos 19, 20, 23 and 24

Run no 19: Ni-IB2A

Compared to the results of run no 11 for the base zeolite, IB-2A, the results of run no. 19 for nickel-exchanged base zeolite, Ni-IB2A, are different in many respects, as outlined below:

- although both catalysts displayed about the same % conversion with respect to synthesis gas and the same total hydrocarbon selectivity, there were

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significant differences in their respective hydrocarbon compositions, shown in Tables 22 and 31, after 240 hours on stream. Methane and C_2-hydrocarbon selectivities were much higher for the nickel-exchanged zeolite while selectivities to C_3-hydrocarbons and C_{5+}-hydrocarbons were much higher for the base zeolite, IB-2A. Therefore, as anticipated, the presence of nickel did indeed significantly favour methanation at the expense of liquid hydrocarbon formation.

- the selectivity to water was slightly higher for the nickel-exchanged zeolite but CO_2 selectivities were the same in both cases.

- nickel-exchanged IB-2A zeolite produced a low olefinic but highly aromatic gasoline (ca 58 wt%). Moreover, the liquid hydrocarbon produced did contain virtually no hydrocarbons higher than C_{12}.

The production over Ni-IB2A zeolite of a highly aromatic liquid hydrocarbon virtually devoid of saturated hydrocarbons higher than C_{12} is indeed very surprising in view of the fact that nickel has always been known as a good methanation and hydrogenation catalyst which would tend to favour the production of saturated paraffinic hydrocarbons over that of aromatics. From a practical point of view, then, the ion-exchange of ZKQ-IB zeolites with nickel affords an elegant yet inexpensive way to produce a high octane premium gasoline of extremely low gum content and very low cloud point from synthesis gas.

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- the selectivity to gasoline was low. In order to improve it at the expense of C_1 and C_2 hydrocarbons, it would be necessary to lower the synthesis reaction temperature by at least 20° C for a % CO conversion of between 65 and 70, reduce the number of milliequivalents of exchanged nickel, and increase the synthesis pressure.

Run no 20: Co-IB2A

There are reasons to believe that at the beginning of the run, the catalyst bed had already began to become partially plugged, as reflected by the rising reactor pressure. The material balance calculated for every 48 hours on stream was always found to be low over the entire duration of the run. Part of the problem can be attributed to carbon laydown, which was not taken into account in material balance calculations. Carbon deposition must have then occured during the pretreatment of the catalyst at a temperature of 375° C, which appears to be too high particularly for cobalt.

In any event, compared to the results of run no 11 for the base zeolite, IB-2A, those of run no 20 for the cobalt-exchanged base zeolite, Co-IB2A, reported in Tables 22 and 32 respectively, showed some differences in the following respects:

- although Co-IB2A displayed a slightly lower overall selectivity to total hydrocarbons than IB-2A, its selectivity to C_{5+}-hydrocarbons (38.72 wt% wrt THC)* was significantly higher than IB-2A's (23.47 wt% wrt THC); as shown in Figure 20, there was

*wrt THC stands for:with respect to total hydrocarbons.

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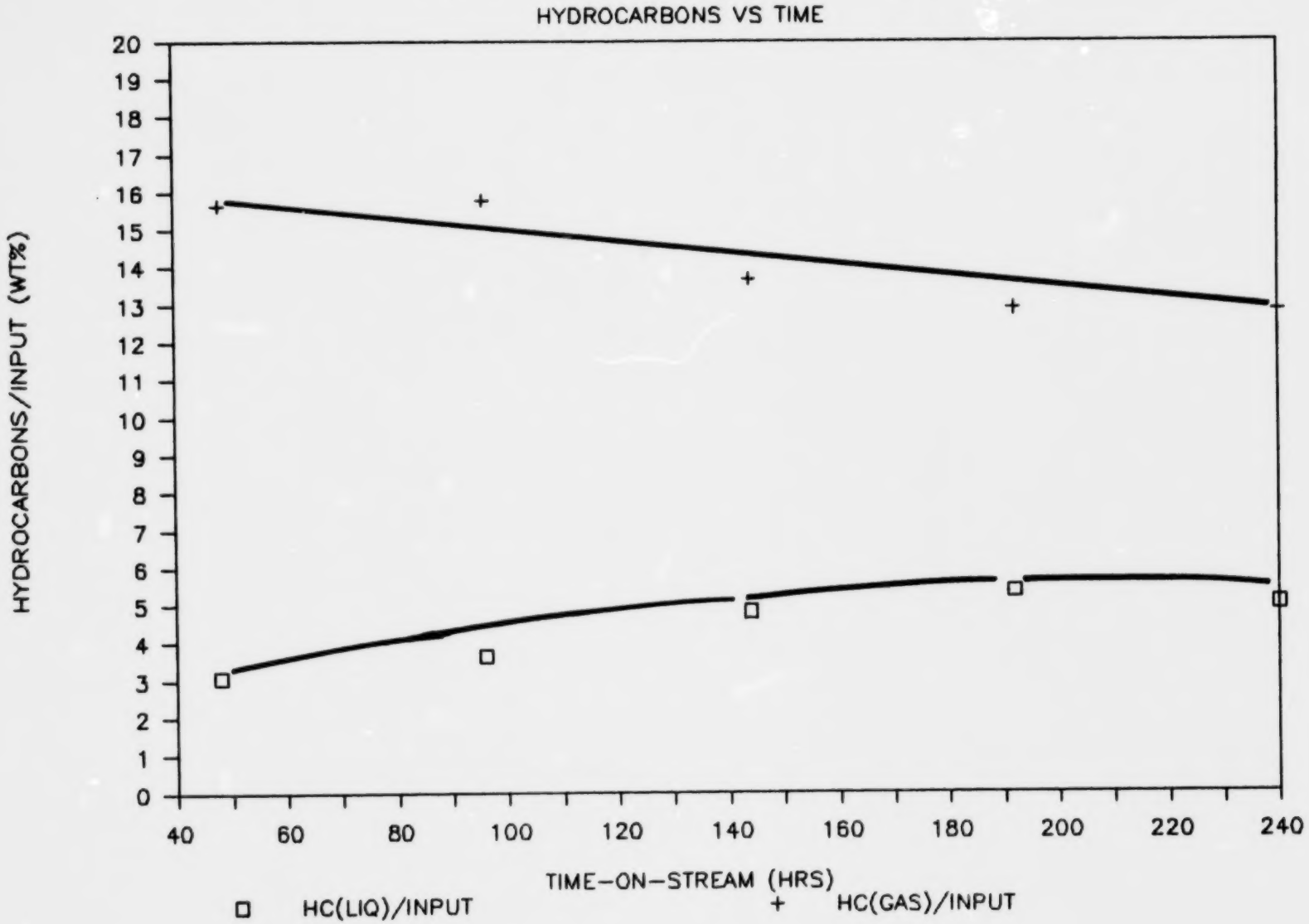
FIG. 20 ZKQCo-IB-20



definitively a trend towards increased selectivity to C_5^+-hydrocarbons for Co-IB2A as a function of time on stream.

- at 240 hours on stream, C_1-C_4 overall selectivities were lower for Co-IB2A (61.28 wt% wrt THC) than for the base zeolite (76.53 wt% wrt THC) and Ni-IB2A (83.92 wt% wrt THC). Of particular note is the surprising fact that Co-IB2A's methane selectivity (29.07 wt% wrt THC) was lower than IB-2A's (39.54 wt wrt% THC). It can therefore be inferred that the presence of cobalt in IB-2A reduces methanation. As in the case of Ni-IB2A, the selectivity to C_3-hydrocarbons for Co-IB2A (2.19 wt% wrt THC) was very much lower than IB2A's (10.21 wt% wrt THC). The presence of cobalt in IB-2A did not suppress the internal shift reaction to a lower extent than expected. Nonetheless, the selectivity to CO_2 for Co-IB2A was 56.92 wt% wrt feed compared to 62.40 wt% wrt feed for the base zeolite, IB-2A, and 62.49 wt% for Ni-IB2A. It can therefore be deduced, based on these results that the presence of nickel in IB-2A does not suppress the internal shift reaction in direct contrast to cobalt. As expected, water selectivity was about 20% higher for Co-IB2A than for the base zeolite.

- as expected, because of the hydrogenation properties of cobalt, the liquid hydrocarbons produced over the cobalt-exchanged catalyst were more paraffinic (41.17 wt% vs 26.89 wt%) and less aromatic (23.39 wt% vs 39.19 wt%) than those produced over the base zeolite. The reason why nickel greatly improves aromatization, whereas the opposite is true for cobalt, is not known, despite the fact that cobalt and nickel are closely related in their properties. Negligible amounts of hydrocarbons higher than C_{12} have been detected

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in the liquid hydrocarbons produced in this run. In summary it appears that cobalt exchanged IB-2A zeolites would be promising catalysts for maximizing liquid hydrocarbon yields.

As far as the operating conditions are concerned, the pretreatment temperature of the catalyst should be lowered considerably to prevent carbon laydown even during pretreatment. The synthesis temperature should likewise be lowered at least by 10° C, and the pressure should not be increased beyond 1600 kPa in order to reduce as much as possible the production of hydrocarbons higher than C_{12}.

Run no 23: La-IB2A + Co

The results of this run are shown in Table 33. The main points of interest which can be made in light of these results when they are compared with those obtained from IB-2A base zeolite are:

- synthesis gas conversion was higher for the lanthanum-exchanged and cobalt-impregnated base zeolite. However, both catalysts gave about equivalent total hydrocarbon selectivities (19.85 wt%/ feed).

- C_1-C_4 selectivities for the modified catalyst were much higher (85.92 wt% wrt THC) than those for IB-2A (78.53 wt% wrt THC) and for Co-IB2A (61.82 wt%). Much of this difference is attributed to the methane selectivity which was 54.78 wt% for the modified catalyst and 39.54 wt% for IB-2A, the values being with respect to total hydrocarbons.

- because of the very high selectivity to C_1-C_4 hydrocarbons of the modified catalyst, its C_{5+}-hydrocarbon selectivity was much lower (13.24 wt%) than that for IB-2A (23:47 wt%) and Co-IB2A (38.72 wt%).

- both La-IB2A + (Co) and IB-2A produced highly olefinic liquid hydrocarbons. The liquid product from the first catalyst was less aromatic (31.45 wt%) than that produced over IB-2A (39.19 wt%).

- hydrocarbons higher than C_{12} were not observed for all practical purposes.

In light of the above results, it appears that the high yield of methane over La-IB2A + (Co) may be attributed solely to the presence of exchanged lanthanum. This inference is based on the fact that IB-2A impregnated with both Co and La actually reduced methanation (run no 24) relative to that of run no 11 for the base zeolite, so that one can conclude that the presence of exchanged lanthanum ions in IB-2A is solely responsible for the high methanation rate over La-IB2A + (Co).

On the basis of the results, one can conclude that exchanging IB-2A with lanthanum and impregnating the exchanged zeolite with cobalt does neither improve the selectivity to C_5^+-hydrocarbons nor the quality of the gasoline relative to the performance of the base zeolite. Moreover, the presence on the base zeolite with 3% impregnated cobalt does not seem to favour the suppression of the internal shift reaction. The catalyst tested in this run does not seem to be promising in syngas conversion.

Run no 24: IB-2A (Co + La)

As can be deduced from the results summarized in Table 34 for this run of IB-2A impregnated with both cobalt and lanthanum, there was a general trend towards increased selectivities to total hydrocarbons, liquid hydrocarbons, and CO_2. After 240 hours on stream, the reactor pressure rose from 1020 kPa to 1700 kPa, reflecting the partial plugging of the catalyst bed. The % synthesis gas conversion was comparable to, or slightly higher than, that of the base zeolite. The CO_2 selectivities were about the same for both catalysts. The major differences between IB-2A (Co + La) and IB-2A in regard to product hydrocarbon selectivities and compositions of the liquid hydrocarbons were:

- the total hydrocarbon selectivity for the modified zeolite was on the whole lower than that for the base zeolite, IB-2A (17.02 wt% vs 19.04 wt% wrt feed at 240 hours on stream). However, its C_5^+-hydrocarbon selectivity was significantly higher than IB-2A's (35.83 wt% wrt THC vs 23.47 wt%).

- with regard to C_1+C_2 selectivity, lower selectivity (43.16 wt% wrt THC) was displayed by the modified catalyst; the base zeolite had a selectivity of 55.29 wt% wrt THC. Methanation was more pronounced on the base zeolite than on the modified catalyst.

- the liquid hydrocarbons produced over IB-2A (Co+La) were in many respects different in composition from

those produced over the base zeolite. Gasoline and distillate with carbon numbers up to 25 were co-produced. The distillate fraction which was rich in normal paraffins constituted about 20% of the liquid hydrocarbon product. Based on PONA analysis, the gasoline fraction was significantly more olefinic (34.65 wt% wrt THC vs 23.01 wt%), vastly less aromatic (6.67 wt% wrt THC vs 39.19 wt%), and more paraffinic than IB-2A's (51.02 wt% vs 26.89 wt%). These results clearly show that the gasoline produced over the modified zeolite is of poor quality on account of its low octane number and its high gum content, attributable to its low aromatic and high olefin contents, respectively.

Compared with the results of run no 20 for the cobalt-exchanged zeolite, Co-IB2A, those obtained in this run, operated at lower pressure, (1020 kPa vs 1633 kPa) were about the same except for the composition of the liquid hydrocarbon produced. The gasoline produced over Co-IB2A was of a better quality than that produced over IB-2A (Co+La) on account of the fact that it contained less olefins (22.77 wt% vs 34.65) and more aromatics (23.39 wt% v/s 6.67 wt%). No distillate was co-produced over the cobalt-exchanged zeolite despite the higher operating pressure.

The major conclusions which can be drawn from the results of this run are:

- the presence of impregnated cobalt and lanthanum on IB-2A brings about the co-production of gasoline which is highly paraffinic (51.02 wt%) and olefinic (34.65 wt%), and extremely poor in aromatics (6.67 wt%), and distillate. Moreover, in contrast with

the lanthanum-exchanged base zeolite, it actually reduces methanation instead of increasing it, as previously anticipated. For some unknown reasons, impregnated lanthanum appears to drastically reduce the aromatization power of the base zeolite.

- in view of the fact that distillate comprising mainly of straight chain paraffins was co-produced along with gasoline at a "relatively" low pressure (1020 kPa), the conduct of the run at a higher pressure, e.g 2000 kPa should enhance the production of distillate by decreasing the G/D (gasoline/distillate) ratio while at the same time favouring the aromatization of the gasoline fraction. On the practical side, increased operating pressure would reduce carbon deposition and increase liquid hydrocarbon yields.

It is recommended that further studies be undertaken on IB-2A (Co+La) with a view to finding ways and means to maximize yields of liquid hydrocarbons, improve quality of the gasoline, and change the G/D ratio to accomodate shift in demand. This catalyst appears to be highly promising.

5.4.4.2 Olefinicity and isomericity of modified IB-2A zeolite

The olefinicity and isomericity of the unmodified zeolites have been dealt with at considerable length earlier. Without much further ado, we present in Table 35 below the values of the olefinicity and isomericity calculated for the four modified IB-2A zeolites. In calculating these values from the data obtained for the analyses of the gas phase, no attempt was made to

TABLE 35

OLEFINICITY AND ISOMERICITY OF METAL-EXCHANGED AND/OR METAL-IMPREGNATED HZKQ-IB ZEOLITES AS A FUNCTION OF TIME

TIME ON STREAM (h)	$=C_2/TOT.C_2$	$=C_3/TOT.C_3$	$=C_4/TOT.C_4$	$iso\text{-}C_4/TOT.C_4$
Catalyst: Ni-HZKQ-IB2A (Nickel exchanged); run 19				
44	0.18	70.97	9.94	32.95
90	0.0	70.00	7.63	34.46
122	0.0	68.75	11.29	37.10
182	0.2	65.63	11.34	37.40
240	0.0	65.63	12.10	37.37
Catalyst: Co-HZKQ-IB2A (Cobalt-exchanged); run 20				
44	0.70	76.20	16.40	36.60
72	1.0	-	17.30	36.80
136	1.0	77.30	20.90	36.00
190	1.6	75.50	24.70	34.30
240	0.9	74.10	27.30	32.60
Catalyst: La-HZKQ+IB2A+(Co) (La-exchanged and Co-impregnated):run 23				
44	0.3	74.51	41.15	13.58
92	0.0	73.91	33.10	16.20
142	0.0	74.47	33.10	15.85
190	0.0	75.00	35.27	16.00
240	0.0	76.00	35.10	18.50
Catalyst: HZKQ-IB2A+(Co+La) (Zeolite impregnated with La & Co: Run 24				
46	1.0	78.79	62.64	7.33
92	0.0	79.70	61.47	5.81
140	0.0	80.00	61.04	5.52
192	0.0	80.28	60.73	5.14
234	0.0	81.43	54.11	9.02
Catalyst: IB2A Base zeolite: run 11				
50	5.19	12.60	26.90	37.60
96	2.46	8.42	23.20	26.60
144	2.05	9.05	24.00	35.64
192	1.73	10.39	25.00	34.77
240	1.71	10.57	25.91	34.01

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include the small and sometimes negligible amounts of light hydrocarbons which had dissolved in the liquid hydrocarbon phase. The values for base zeolite IB-2A are included in the table to facilitate comparison of results.

As seen in Table 35, the modification of the base zeolite either by ion-exchange or impregnation with metal(s) may have vastly different effects on the olefinicity and isomericity, depending on the modification technique used. Thus, using the results for base zeolite IB-2A as reference, the exchanged base zeolites, Ni-IB2A and Co-IB2A, produced the following results:

- both exchanged zeolites reduced the $C_2^=$ olefinicity to virtually negligible values; this is due to their extremely low ethylene selectivities on the one hand, and on the other, to their relatively much higher ethane selectivities. Moreover, both metals are known for their good hydrogenating properties, such that, once produced, ethylene is converted to ethane.

- as regards $C_3^=$ olefinicity, both exchanged nickel and cobalt increased it to about 75 to 80wt% relative to that of the base zeolite which was about 10 wt%.

- exchanged nickel actually reduced $C_4^=$ olefinicity by one half whereas exchanged cobalt had no significant effect.

- exchanged nickel and cobalt did not affect the isomericity of IB-2A.

With lanthanum-exchanged and cobalt-impregnated base zeolite, La-IB2A+(Co), and lanthanum and cobalt-impregnated base zeolite, IB2A+(Co+La), the following results were obtained:

- both modified zeolites reduced the $C_2^=$ olefinicity to zero; ethylene was simply not detected in the gas whereas ethane selectivity was about 4.5 wt% and 2.7 wt% wrt feed for the La-exchanged zeolite and the La-impregnated zeolite respectively.

- $C_3^=$ olefinicity increased 7.5 to 8.0 times over that of the base zeolite with both modified zeolites.

- both modified zeolites also increased $C_4^=$ olefinicity but decreased the C_4 isomericity.

As a rule, the total C_2-C_4 olefinicity of the modified base zeolites decreases in the following order:

Fully impregnated zeolite exchanged and impregnated zeolite exchanged zeolite
e.g IB-2A+(Co+La)>La-IB2A+(Co)>Co-IB2A>Ni-IB2A

The reverse order applies as far as C_4 isomericity is concerned
e.g Ni-IB2A>Co-IB2A>La-IB2A+(Co)>IB2A+(Co+La)

On the basis of the results of PONA analyses of C_5^+-hydrocarbons, it can be concluded that only exchanged nickel significantly increased aromatics selectivity while both lanthanum and cobalt actually reduced it.

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5.4.4.3 Analysis of aqueous phase of runs no 19, 20, 23 and 24

Product water samples from each of the runs were analysed by gas chromatography for their contents in oxygenates. The results are reported for product water samples collected at 240 hours on stream. As seen in Table 30 section 5.4.3.5, aliphatic alcohols and ketones up to C_5 in negligible amounts were detected in some samples while in others no alcohols were detected. Only the sample from run no. 15 contained methanol to the extent of 1.4 wt%, which is by no means negligible. Acetone was the only aliphatic ketone that was present in all samples. Except for runs no 10, 12 and 20 whose water samples contained 0.36 wt%, 0.42 wt% and 0.64 wt% acetone, all the remaining samples had acetone contents considerably less than 0.1 wt%.

5.4.4.4 Synthesis reaction on IB-1B zeolite: Run no. 18

ZKQ-IB1B crystalline ironborosilicate zeolite was synthesised in the same manner as the other base zeolites except that the source of boron used was boric acid instead of an alkali tetrahydroborate. For some unclear reasons, the time required to effect crystallization of the zeolite was longer than that taken for the other base zeolites. Although no data are available regarding its relative degree of crystallinity, it is quite probable that it was low.

The results of run no 18 given in Table 25 (Appendix A) show that IB-1B had relatively low % synthesis gas conversion and its selectivity to liquid hydrocarbons was extremely low while its C_1 to C_4 selectivity was very high. Its water selectivity was unusually high (9.71 wt% wrt feed) at 34.17% CO conversion.

Its low activity which did not seem to pick up after 265 hours on stream may be attributed to two factors: its low relative degree of crystallinity (to be confirmed) and its very high residual sodium content (8600 ppm). The unacceptably high residual sodium content in IB-1B is definitely due to the unfortunate result of insufficient washing of the zeolite and/or to the occlusion of sodium in amorphous material from which it can probably be removed only with great difficulty. Its high olefinicity and low C_4 isomericity are comparable to those of another base zeolite, IB-4A, which also had high residual sodium content and low relative degree of crystallinity.

5.4.4.5 Compositions of gasoline samples from selected runs

In an effort to give a representative cross-section of the composition spectrum of gasolines which may be obtained over modified and unmodified IB-2A zeolites, the detailed results of PONA analyses of gasoline samples from selected runs over 5 catalysts have been compiled in Table 36 for comparative interpretation, using IB-2A base zeolite as a reference whenever warranted.

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TABLE 96

TYPICAL COMPOSITIONS OF GASOLINE SAMPLES TAKEN AT 192 HOURS ON STREAM

CATALYSTS	IB-2A	IB-4A*	Ni-IB2A	Co-IB2A	IB-2A+(Co + La)*
RUN NO	11	16	19	20	24
			WT%		
C_5					
n-pentane	0.047	-	0.170	0.789	0.703
i-pentane	0.036	-	0.144	0.659	0.170
methyl butane	0.059	0.076	0.069	0.765	2.702
pentadiene	-	-	-	-	0.100
pentene	-	-	-	0.154	0.523
TOTAL C_5	0.142	0.076	0.383	2.367	4.198
C_6					
n-hexane	0.415	0.260	0.504	1.714	2.048
cyclo-hexanes	-	-	0.039	0.033	-
methyl pentanes	0.590	-	0.873	2.181	0.727
methyl cyclo-pentanes	0.205	-	0.358	0.311	0.048
C_6-olefins	0.420	0.840	0.130	1.290	6.380
TOTAL C_6	1.772	1.100	1.904	5.529	9.203
C_7					
n-heptane	0.879	1.904	0.718	2.321	3.374
branched G_7-P	2.841	0.520	2.367	4.312	2.757
dimethyl cyclo-C_5	0.491	0.143	0.986	0.834	0.360
ethyl cyclo-C_5	-	-	0.401	0.259	-
methyl cyclo-C_6	-	-	0.872	0.598	0.029
C_7-olefins	2.720	4.970	0.34	3.570	10.02
TOTAL C_7	6.930	7.537	5.684	11.894	16.54
C_8					
n-octane	1.680	6.660	1.376	2.743	5.511
branched C_8-P	6.875	1.873	4.690	6.268	3.210
C_8-olefins	7.360	7.320	1.160	5.310	7.550
C_8-naphtenes	4.372	1.730	3.720	3.33	1.81
TOTAL C_8	20.287	17.583	10.946	17.651	18.081
C_9					
n-nonane	0.707	8.485	0.389	1.669	5.183
branched C_9-P	5.137	3.764	5.200	6.663	4.779
C_9-olefins	8.333	5.600	2.213	5.807	4.306
C_9-naphtenes	3.618	4.839	6.520	6.229	3.657
TOTAL C_9	17.795	22.688	14.380	20.368	17.925

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TABLE 36 (continuation)
TYPICAL COMPOSITIONS OF GASOLINE SAMPLES
TAKEN AT 192 HOURS ON STREAM

CATALYSTS	IB-2A	IB-4A*	Ni-IB2A	Co-IB2A	IB-2A+(Co + La)*
RUN NO	11	16	19	20	24
			WT%		
C_{10}					
n-decane	-	7.391	2.305	0.760	4.353
branched C_{10}-P	4.733	5.521	4.110	6.782	5.288
C_{10}-olefins	3.428	2.566	1.242	2.093	1.478
C_{10}-naphtenes	1.362	2.147	1.244	1.171	1.143
TOTAL C_{10}	9.769	17.625	6.902	10.806	12.532
C_{11}					
n-undecane	0.242	8.998	0.229	0.329	4.695
branched C_{11}-P	2.311	3.044	2.904	2.826	1.744
C_{11}-olefins	0.969	0.591	0.659	0.536	0.263
TOTAL C_{11}	3.522	12.633	3.792	3.691	6.702
C_{12}					
n-docecane	-	8.193	-	-	3.795
branched C_{12}-P	0.873	2.291	1.822	0.900	1.839
C_{12}-olefins	-	0.100	0.210	0.074	0.162
TOTAL C_{12}	0.873	10.584	2.032	0.974	5.796
C_{13}					
C_{13}-olefins	-	0.956	0.194	-	0.162
TOTAL C_{13}	-	0.956	0.194	-	5.796
AROMATICS					
A_6					
Benzene	0.175	0.068	0.059	0.261	0.154
A_7					
Toluene	1.485	0.283	1.693	0.859	0.306
A_8					
Ethyl benzene	0.842	0.286	1.178	0.430	0.154
O-xylene	0.951	0.151	1.268	0.480	0.255
M-xylene	4.950	0.686	6.170	2.303	0.502
P-xylene	1.978	0.227	1.822	1.216	0.218
TOTAL A_8	8.721	1.350	10.438	4.429	1.129
A_9					
O-ethyl toluene	0.153			-	-
M-ethyl toluene	9.210	0.443	12.329	4.834	0.545
P-ethyl toluene	5.008	-	5.721	2.788	0.347
Trimethyl benzene (1,2,3)	-	0.111	-	0.095	0.039
Trimethyl benzene (1,2,4)	2.899	0.271	5.118	1.447	0.293
Trimethyl benzene (1,3,5)	-	0.475	0.480	0.785	0.324
n-propyl benzene	0.299	0.733	1.773	1.282	0.394
i-propyl benzene	0.111	0.188	0.097	0.071	0.076
C_9-aromatics (unidentified)	0.575	1.119	-	-	0.333
TOTAL A_9	18.255	3.340	25.518	11.302	2.351

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TABLE 36 (continuation)
TYPICAL COMPOSITIONS OF GASOLINE SAMPLES
TAKEN AT 192 HOURS ON STREAM

CATALYSTS	IB-2A	IB-4A*	Ni-IB2A	Co-IB2A	IB-2A+(Co + La)*
RUN NO	11	16	19	20	24
			WT%		
A_{10}					
Tetramethylbenzene (1,2,4,5)	0.618	0.212	1.429	0.555	0.097
Tetramethylbenzene (1,2,3,5)	-	-	0.047	-	0.036
n-butyl benzene	1.374	0.230	1.841	1.221	0.227
i-butyl benzene	0.579	-	0.070	0.124	-
t-butyl benzene	-	-	0.054	-	-
methyl n-propyl benzene	4.137	0.441	6.105	2.245	0.318
methyl i-propyl benzene	0.166	0.115	0.706	-	0.123
diethyl benzenes	0.298	0.693	0.603	0.376	0.389
dimethyl ethyl benzenes	0.727	0.130	0.287	0.291	0.199
C_{10}-aromatics (unidentified)	0.770	1.186	1.891	1.126	1.071
TOTAL A_{10}	8.669	3.007	10.44	6.493	2.461
A_{11}					
methyl butyl benzene	0.108	-	0.338	0.069	0.100
C_{11}-aromatics (unidentified)	1.637	1.072	2.667	2.197	0.925
TOTAL A_{11}	1.745	1.072	3.005	2.266	1.025
A_{12}					
Triethylbenzenes	-	0.129	-	-	0.093

* Both IB-4A and IB2A+(Co + La) co-produced gasoline and distillate.

The salient points which may be derived from an examination of the results are:

- The light-end C_5 and C_6 contents of the gasolines increase in the following order:

  IB2A+(Co+La) > Co-IB2A > Ni-IB2A > IB-2A > IB4A

  The relative high residual sodium content in IB4A may help explain why its light-end hydrocarbon selectivity was low.

- as mentioned before, presence in, or the addition of, alkali metal to iron catalysts shifts the product to higher molecular weight range. This is observed for IB-4A, which gave a gasoline with the highest straight chain C_7 to C_{12} hydrocarbon content, as shown in the following order of decreasing straight chain paraffin selectivity:

  IB4A > IB2A+(Co+La) > Co-IB2A > Ni-IB2A, IB2A

  Because of its reduced acidity IB4A yielded a gasoline very poor in aromatics. It is to be noted that distillate constituted an important fraction of the liquid product.

- Co-IB2A yielded a gasoline that had the highest branched paraffin C_6-C_{11} content. The content in branched paraffins decreased in the following order Co-IB2A > IB-2A > Ni-IB2A > IB2A+(Co+La), IB-4A.

- compared to the total olefin content of IB2A-gasoline (23.29 wt%), that of Ni-IB2A was 6.22 wt%.

Thus, as noted before, exchanged nickel considerably reduced the total olefinicity of IB-2A.

On the other hand, Co and La-impregnated IB2A yielded a gasoline with the highest total olefin content (34.65 wt%). Thus, the olefinicity decreased in the following order.

IB2A+(Co+La) > IB4A > IB-2A > Co-IB2A $\gg$ Ni-IB2A

- Quite surprisingly, exchange nickel significantly increased the aromatic content of IB2A-gasoline from 39.05 wt% to 53.74 wt%. On the other hand, as expected, exchanged Co decreases the aromatic content of IB2A gasoline to 25.97 wt%. Thus, having a low olefinicity and a high aromaticiy, Ni-IB2A produced the best premium gasoline. On the order hand, IB2A + (Co+La), which co-produced gasoline and distillate, yielded the poorest quality gasoline. The aromaticity of the catalysts decrease in the following order.

Ni-IB2A > IB-2A > Co-IB-2A > IB4A= IB2A+(Co+La)

In light of the above, it can be inferred that the properties of IB4A and IB2A+(Co+La) are virtually equivalent in terms of their selectivities to the various hydrocarbons both in the gasoline and distillate boiling range. Co-IB2A is more closely related to the base zeolite than Ni-IB2A.

- Finally, in terms of C_5^+ selectivity (distillate plus gasoline) we have the following order with

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decreasing selectivity (based on results at 240 hours on stream).

Co-IB2A > IB2A+(Co+La) > IB2A, IB4A > Ni-IB2A.

5.4.4.6 Tests of longer duration in bigger reactors at Queen's University

The base zeolite ZKQ-IB2A and the Ni-exchanged IB2A were selected for longer duration tests (3 weeks) in modified Berty reactors of 100 to 200 mL capacity. Consistent with the gradual phasing-out of the incorporation of lead alkyls in gasoline, Ni-IB2A was selected on the basis of the fact that it yielded the best quality gasoline during run no 19 in the small reactor. The report prepared by Prof. B. Wojciechowski is included in Appendix C in its entirety.

Gasoline characterization

The results of PONA analyses carried out at CRIQ, of samples of the liquid hydrocarbons collected over the entire duration of the tests are given in Table 37. Physical characterization, albeit limited in extent, was carried out on the limited available quantities of gasoline. The results are reported in Table 38.

Contrary to expectations, the results of the tests performed at Queen's University are disappointing particularly in regard to the low CO conversions observed in both tests and the relatively poor C_5^+ hydrocarbon selectivities of both catalysts.

TABLE 37

GASOLINE ANALYSIS

SAMPLE	IB2A wt%				Ni-IB2A wt%			
	P	O	N	A	P	O	N	A
2	23.33	39.65	13.57	23.46	7.72	2.92	4.9	84.46
3	21.50	27.73	9.04	11.74	14.12	10.23	11.29	64.36
4	20.34	58.54	8.67	12.44	13.98	10.71	12.01	63.30
5	20.72	56.43	9.35	13.50	14.47	11.93	11.94	61.65
6	21.78	53.18	10.27	14.77	-	-	-	-
7	20.95	57.52	9.11	12.42	15.53	14.11	12.59	57.76
8	24.71	52.53	10.16	12.60	25.77	19.56	15.02	39.65
9	25.53	53.25	8.64	12.58	-	-	-	-
10	24.05	54.49	9.47	11.99	11.99	20.32	15.38	38.81
11	25.10	52.21	9.88	12.81	12.81	19.46	14.49	43.06
12	24.97	52.41	9.52	13.10	13.10	17.04	14.34	47.12

However, the results of PONA analyses of Ni-IB2A gasoline shown in Table 37 do confirm our findings that exchanged Ni profoundly affects the chemical composition of IB2A-gasoline by increasing its aromatics content and reducing its olefinic content. In terms of composition and residual sodium content both catalysts did not essentially differ from their counterparts when tested in small reactors, as indicated in Tables 3 and 5.

As shown in Table 37 the olefin (54 wt%) and the aromatic contents (10 wt%) of IB2A-gasoline (Berty) were entirely different from those reported earlier for the gasoline obtained from the same base zeolite in small fixed-bed reactor (ca 23 wt% olefins and ca 39 wt% aromatics). This vast difference in composition may partly be attributed to the residual sodium content of both catalysts: 0.33 wt% Na_2O for IB-2A tested in Berty reactor v/s 0.10 wt% Na_2O for IB-2A tested in small reactor.

As seen in Table 38, both catalysts which yielded gasolines low in light-end hydrocarbons had 10% volume distilled over at 81.5° C and 88.0° C while it is 57° C for a non-leaded gasoline. Furthermore, because of the virtual absence of C_4-hydrocarbons such as n-C_4 or i-C_4 the gasolines had very low Reid vapour pressures. The addition of anti-oxidant to, and/or the mild hydrogenation of, the freshly gasoline prepared, may obviate this quality limitation.

It is believed that the principal reason for the poor activity observed for the catalysts rests largely on the method and conditions of pretreatment. With the

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TABLE 38

PHYSICAL CHARACTERIZATION OF GASOLINE

	2A (°C)	Ni-2A (°C)	GASOLINE (ASTM) (°C)
DISTILLATION			
Initial point	29.6	30.0	
5%	63.5	71.0	
10%	81.5	88.0	57
20%	100.0	108.5	
30%	126.0	120.0	
40%	130.5	128.5	
50%	139.5	138.0	118
60%	148.5	147.0	
70%	156.5	157.0	
80%	168.0	169.0	
90%	186.0	183.5	185
95%	214.0	210.5	
Final point	223.0	214.5	
Recovered	96.5	97.0	
Residue	3.0	3.0	
Lost	0.5	0	
Reid pressure (kPa)	39	26	83.5
Gum (mg/100 c.c.)	574	19.6	70
Cloud pt (°C)	1	-55	

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benefit of hindsight it seems that prior reduction of the catalyst in flowing pure hydrogen at a lower temperature for an extended period followed by carbiding in pure CO or syngas would be more appropriate. As has been mentioned, elemental carbon deposition from CO dissociative adsorption thereon appears to be favoured in the presence of hydrogen.

Of particular note are the drastic reduction of the gum content of the gasoline and the tremendous improvement of its cloud point, brought about simply by exchanging the base zeolite with nickel (Table 38).

It is not known whether the presence of zinc as a contaminant (less than 150 ppm see Table 5 in Ni-IB2A) is sufficient as to be the main cause of the aromatization properties of Ni-IB2A. Exchanged zinc has been implicated in improving the aromaticity of ZSM-5.

The fact that Ni-IB2A does yield a high quality gasoline is important in another respect: it can be employed under optimum operation conditions in upgrading the total hydrocarbon effluent from a conventional F-T catalytic reactor in a dual reactor or follow bed system.

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5.4.4.7 Comparison with published results

Table 39 compares the results obtained from IB-1A, IB-2A, Ni-IB2A and Co-IB2A with those obtained with other catalysts by workers in the field. The results for IB-4A and IB2A(Co+La) were left out on purpose because they co-produced gasoline and diesel. As can be seen in Table 39, important data have been left out by some workers.

We may infer, from the results reported in the Table, the following:

- all ironborosilicate catalysts displayed the highest CO_2 selectivities and the lowest H_2O selectivities.

- based on the approximately equivalent $CO+H_2$ conversions of Co-IB2A and Fe-HZSM5 (ref. 3), the C_1-C_4 selectivity of the former (2.41) is lower than that of the latter (15.7). The higher C_1-C_4 selectivity of Fe-HZSM5 may partly be due to the higher synthesis temperature (371° C) but the higher pressure (3550 kPa) should counteract this to some extent by favouring formation of liquid hydrocarbon.

- except for the results reported for ref. 4 and 5, the aromatic contents of IB-gasolines are by and large higher than those reported in the remaining references.

  As anticipated, the gasoline produced on MnFe-silicalite is very poor in aromatics and very rich in olefins on account of its low acidity.

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TABLE 39
RESULTS OF VARIOUS REPORTED SYNGAS CONVERSION TESTS

CATALYSTS	IB-1A	IB-2A	Ni-IB2A	Co-IB2A	5.8%Fe/ZSM5 (1)	16%Fe/ZSM5 (2)	Fe-HZSM5 (3)	3%Fe-HZSM5 (3)	MnFe-Si1 (4)	MnFe-ZSM5 (4)	3.1%Fe/ZSM5 (5)
T, °C	310	310	310	310	300	300	371	371	310	310	300
P, kPa	1050	1050	1123	1550	1380	1380	3550	1827	1215	1215	2140
GHSV H^{-1}	300	300	390	454	1600	1000	30 sec	15 sec	340	350	1500
Time. h	337	96	144	192	43	-	-	-	-	-	-
CO Conv., %	94.17	90.29	96.12	97.23	51.5	54.00	98.40	19.70	-	-	7.5
H_2 Conv., %	86.29	79.56	79.76	77.06	57.1	62.00	72.30	12.00	-	-	15.0
CO H_2 Conv., %	-	-	-	-	-	-	-	-	87	78	-
PROD. DIST.											
CO_2	72.83	73.09	72.24	71.56	51.2	52.0	-	-	-	-	24.3
H_2O	4.31	4.73	5.61	6.78	19.0	17.3	-	-	-	-	33.3
Hydrocarb.	22.86	22.18	22.15	21.66	29.8	30.7	25.5	8.1	-	-	42.2
SELECTIVITY											
C_1-C_4/C_5^+	4.48	3.42	7.78	2.41	0.58	1.86	15.7	4.2	-	-	3.7
PONA ANALYSIS (wt%)											
Paraffins	33.79	31.50	27.50	41.45	-	-	-	-	34.5	54.1	-
Olefins	26.77	25.35	4.59	19.82	-	-	-	-	59.9	0.0	-
Naphtenes	10.72	11.15	16.64	12.76	-	-	-	-	-	-	-
Aromatics	28.72	31.99	51.67	25.97	14.0	9.0	15.0	24.6	5.6	45.9	66.1

N.B.: H_2: CO RATIOS WERE 1:1 IN ALL CASES

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6.0 SUMMARY, OBSERVATIONS AND RECOMMENDATIONS

6.1 Recapitulation

Within the framework of this cost-shared project all the tasks are summarised below in the order they were carried out.

- preparation and characterization of five ironborosilicate base zeolites, which have been described at considerable lengths in the appropriate section of this report;

- in the absence of any standard activation procedures for a novel type of synthesis catalysts such as crystalline ironborosilicate zeolites, attempts were to be made at finding the "optimum" pretreatment conditions for a typical zeolite such as IB-1A;

- selecting the operating conditions under which all synthesis tests would be carried out;

- conducting synthesis gas conversion tests, each for a minimum duration of 240 hours, on the prepared base zeolites designated as IB-1A, IB-2A, IB-3A, IB-4A, and IB-1B; one additional test which was not planned was performed on IB-1A which was steam-activated prior to carbiding;

- on the basis of the results obtained from the various runs, one of the afore-mentioned zeolites was selected for further longer duration tests and for modifications; the selected zeolites was IB-2A;

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- in an attempt to reduce the high selectivity to CO_2 observed with all the IB base zeolites and to maximize selectivity to liquid hydrocarbons, IB-2A base zeolite was modified by way of ion-exchange and/or impregnation with Ni, Co, and La. Thus, nickel-exchanged zeolite (Ni-IB2A), cobalt-exchanged zeolite (Co-IB2A), lanthanum-exchanged and cobaltimpregnated base zeolite (La-IB2A+(Co)), and lastly, cobalt and lanthanum-impregnated base zeolite (IB-2A+(Co+La)), were prepared and tested.

- all products in the non-condensed phase, in the aqueous phase, and in the organic phase were analysed.

6.2 Obsevations and Conclusions

Based on our own findings and on the results obtained by Wojciechowski (see Appendix C), it can be said with a fair degree of certainty that heavy carbon deposition took place readily on the catalysts even during pretreatment, which in the majority of cases, led to gradual plugging of the reactor beds. The time taken to reach steady-state conditions during synthesis runs was relatively long in all cases.

It is believed that reduction, carbiding and synthesis were all taking place simultaneously. With the benefit of hindsight, it is now believed that the rather high pretreatment temperature (375°C) was partly responsible for bringing about heavy initial carbon deposition in view of the very high activity of the catalysts on which the Boudouard reaction appears to take place without much difficulties. Pretreatment of the

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base zeolite in the presence of synthesis gas at a lower temperature but for longer periods of time is therefore indicated. Aside from this, however, it is recommended that, in any future studies on the pretreatment of crystalline ironborosilicate zeolites, the latter be first reduced at fairly high temperatures in flowing pure hydrogen before being carbided at temperatures below 350°C either in carbon monoxide alone and then in synthesis gas or in synthesis gas alone.

Despite the fact that in the majority of cases the reactor beds became gradually plugged as a result of heavy carbon deposit and/or the disintegration of the catalyst pellets into fines, all the catalysts nevertheless displayed extremely high feed gas conversions throughout the runs. This, then, brings one to conclude that their activities must have been very high indeed and that the maintenance of such high activities in spite of the "massive" carbon deposits suggest that they would most probably have long life cycles and hence, useful long lives. The bulk of such "massive" carbon deposit is most probably made of filamentous or vermicular carbon which has been shown to have little deleterious effects on catalytic activities. The presence of such form of carbon can be substantiated by SEM. On the basis of past experience with regenerability of "coked" titanoborosilicate zeolites, it is anticipated that the re-activation of ZKQ-IB zeolites via standard oxidation combustion of carbon deposits will be easy.

Of the five base zeolites tested, all but IB-1B gave high CO conversions, some higher than others. The following sequence gives their activity levels in decreasing order:

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IB-2A IB-1A (steam-activated) IB-1A IB-3A IB-4A IB-1B

The differences noted in their activities as well as in their selectivities have been linked to the following main factors:

- the presence of residual sodium in the zeolite not only affects its activity but also its total hydrocarbon selectivity and its olefinicity, isomericity, as well as its aromatization and alkylation capabilities. Moreover, when the residual sodium is relatively high, the molecular weight distribution of the hydrocarbons is shifted to higher values; it is likely that distillate production over IB-4A is partly attributable to high residual Na contents. This profound effect of residual sodium (of acitidy) can find important applications in controlling product selectivity, and quality;

Thus, in order of decreasing olefinicities of the catalysts, we have the following sequence:

IB-4A > IB-3A > IB-1A > IB-2A

The reverse order has been observed with C_4 isomericity, aromatization and alkylation of benzene nucleus for production of alkylated benzenes. Thus, the lower the sodium content, that is the higher the acidity, the higher are the isomericity, aromatization and alkylation capabilities of the zeolite.

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- a low degree of crystallinity, which is often observed with zeolites high in residual sodium contents, (sodium which is removed with extreme difficulties) generally leads to lower total hydrocarbon and C_5^+-hydrocarbon selectivity;

- a high B-E-T surface area, often observed with highly crystalline zeolites, is conducive to high hydrocarbon selectivity.

IB-2A base zeolite was selected as the most promising base zeolite for further testing and modifications on account of the fact that it had the highest relative degree of crystallinity and BET surface area and the lowest residual sodium content, which, as has been mentioned above, are all conducive to high activity and C_5^+-hydrocarbon selectivity particularly towards gasoline range products rich in aromatics and branched hydrocarbons. On the other hand, IB-1B showed extremely poor CO conversion (less than 15%) and low total hydrocarbon selectivity, which are attributable to its low degree of crystallinity and unusually high residual sodium content (0.8 wt%).

Of particular interest is the fact that any variation in the iron content of the zeolite within the limits set by the lowest and highest iron contents used in this project did not seem to affect the activity of the zeolite. In other words, a zeolite containing 12 wt% Fe_2O_3 for instance would not necessarily display a higher activity than one containing 6 wt% Fe_2O_3.

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Steam-activated IB-1A base zeolite slightly improved the total hydrocarbon selectivity of IB-1A but produced a gasoline richer in paraffins and poorer in aromatics.

Because of their shape-selective properties, all of the base zeolites except IB-4A, which happen to contain the highest amount of sodium, selectively yielded liquid hydrocarbons no higher than C_{12}. IB-4A co-produced distillate and a gasoline poor in aromatics but very rich in olefins. By controlling residual sodium content and increasing the operating pressure, it will be possible to produce both diesel and gasoline in proportions that could be adjusted to meet shifts in demand. There is apparently a certain residual sodium content threshold beyond which the formation of diesel is highly favoured. Mainly concentrated in the C_7 to C_{10} carbon range, the olefins present in IB-4A gasoline can be dimerized, if required, to distillate range products over zeolites of very low acidities via the application of high pressures (ca 1500 psi). The gasolines produced over the base zeolites all had high olefin contents. High octane gasoline production was favoured over zeolites of very low residual sodium contents.

The results obtained from the various runs on the four

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modified IB-2A zeolites have shown quite convincingly that by simply doping/exchanging and/or impregnating IB-2A base zeolites with Ni, Co, and La, profound changes are brought about, particularly in regard to the hydrocarbon product distribution. From these results, the following conclusions have been drawn:

- the suppression of the internal shift reaction by doping IB-2A with cobalt was lower than expected;

- compared to IB-2A base zeolite, both Co-IB2A and IB-2A + (Co+La) displayed higher C_5^+-hydrocarbon selectivities. However, there was co-production of gasoline and distillate on the latter. The gasoline, which constituted about 80% of the liquid product was very rich in olefins (34.65%) and in paraffins (51%) but extremely poor in aromatics (ca 6.5%). Co-IB2A yielded a gasoline that was more paraffinic and less aromatic than IB2A-gasoline. A major portion of the paraffinie fraction, however, was constituted by highly branched paraffins with high octane number;

- lanthanum-exchanged and cobalt-impregnated base zeolite had extremely poor C_5^+-hydrocarbon selectivity and hence, very high C_1-C_4 selectivity (ca 85%). This has been attributed to the direct influence of exchanged lanthanum which promoted methanation to the extent that methane constituted 55 wt% of the total hydrocarbons. The catalyst had marginal effect on olefination. Thus, the manner in which the base zeolite is modified such as by ion

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exchange or impregnation does affect hydrocarbon selectivity, hence product quality. La-IB2A+(Co), then, is not considered a promising catalyst on account of its poor liquid hydrocarbon selectivity.

- thus, Co-IB2A zeolite appears to be a promising catalyst for maximising gasoline yield. Most of the olefins in IB-2A+(Co+La) gasoline are concentrated in the C_6-C_{12} range; they can be dimerized or oligomerized to boost distillate yield. It is concluded that by controlling Co/La ratio it will be possible to produce both premium quality diesel and/or jet fuel or blending stock thereof;

- in contrast to Co-IB2A, exchanged nickel had no effect on the suppression of the internal shift reaction;

- Ni-IB2A yielded a gasoline which had a much lower olefin and a much higher aromatic contents than IB-2A-gasoline. Thus, the ion-exchange of ZKQ-IB zeolites with nickel affords an elegant yet inexpensive means of producing a high octane premium gasoline of extremely low existant gum content and potential gum content and very low cloud point. Another perhaps important outcome of this finding is the potential application of nickel-exchanged iron-borosilicate zeolites operated under optimum process conditions to the upgrading of the total effluent from a conventional F-T catalytic reactor into high octane gasoline.

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In conclusion, it can be said with some justification that this project has clearly demonstrated that both modified and unmodified ZKQ-IB crystalline ironborosilicate base zeolites are promising multi-functional catalysts in synthesis gas conversion reactions for the specific production of gasoline or of gasoline and distillate fuels in proportions that can be adjusted to meet shifts in demand by fine tuning the composition of the catalyst and by controlling process conditions. ZKQ-IB ironborosilicate zeolites which are believed to be the first Canadian proprietary multi-functional synthesis gas conversion zeolitic catalysts have great potentials in upgrading conventional F-T products in dual-reactor systems.

6.3 Recommendations

The results obtained in this project have no doubt been extremely promising and informative. From them, appropriate inferences have been drawn and passing mention has been made in regard to the potential applications of ZKQ-IB crystalline ironborosilicate zeolites in various existing commercial hydrocarbon conversion operations, particularly in upgrading processes. It is common knowledge to those working in the catalysis field that the development of a catalyst is usually a long-drawn undertaking. With this in mind and on the basis of the results obtained, it is recommended that further studies be done on ZKQ-IB zeolites in the following areas of research and development:

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1. Pretreatment of ZKQ-1B zeolites

Consistent with what has been said in this report, the establishment of a pretreatment procedure for ZKQ-1B zeolites is of vital importance, for upon it will depend to a rather great extent subsequent performance in synthesis reactions. It is our belief that the pretreatment procedure we have used has had only mitigated success. Partial plugging of the reactor bed during pretreatment which appears to be a direct consequence of the rather high temperature employed was observed.

It is therefore proposed that a systematic study of the effect of temperature on carbon formation during pretreatment be carried out. Secondly, the pretreatment involving the reduction of the catalyst in flowing pure hydrogen followed by carbiding either in pure CO or in synthesis gas should be studied. The use of techniques such as temperature-programmed reduction (TPR) and thermogravimetry are recommended. All of these techniques, will give the "optimum" temperature of pretreatment.

2. Effect of sodium concentration on activity and selectivity of ZKQ-1B zeolites

Much has been said about the profound influence of residual sodium on hydrocarbon product distribution. Coupled with the application of high pressure which is known to favour the formation of higher molecular weight products, the "doping" of the base zeolite with graduated amounts of sodium

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or potassium should enable the location of the optimum concentration range for maximizing distillate production while minimizing production of aromatics. Based on the available data, the distillate would mainly comprise of premium grade diesel following mild hydrogenation. If required the catalyst may be optimised for the co-production of gasoline and diesel.

In view of the "predicted" shortage of good feedstock for premium diesel production, we believe a systematic study of the role of sodium in ZKQ-IB zeolites for the directed production of diesel from syngas is indicated.

3. Role of exchanged cobalt on selectivity to liquid hydrocarbons

Cobalt-exchanged ZKQ-IB zeolite has been found to increase selectivity to gasoline range liquid hydrocarbons containing about 25 wt% aromatics, 32 wt% branched paraffins and 20 wt% olefins. In order to increase the aromatic and decrease the olefin contents of the gasoline and to maximize yield, it is proposed that a study of the role of cobalt concentrations in the exchanged as well as the impregnated form on the activity and selectivity of the zeolite be undertaken on the one hand and on the other, of the beneficial effect which the graduated doping with nickel or the cobalt-exchanged zeolite may have on the quality of the gasoline.

4. Production of jet fuel and/or blending stock thereof

The co-production of a poor quality gasoline which is extremely low in aromatics and very rich in olefins and of distillate over cobalt and lanthanum-impregnated base zeolite is worth mentioning because it is believed that the olefins present in the gasoline fraction can be oligomerised further into distillate, which can subsequently be hydrogenated into branched paraffins. Given the very low aromatic content whose formation can be minimized further by certain modification to the catalyst, it is therefore entirely possible to convert at least 60 wt% of the C_5^+-hydrocarbons into premium jet fuel. R & D in this area is recommended.

5. Study of the effect of binders on ZKQ-IB performance

In view of the very high activty of ZKQ-IB zeolites and of their potentials to attain commercial exploitation, there is a need to see what will be the effect, if any, of binders on their performance as synthesis catalysts. Industrial zeolite catalysts are composed of the zeolite component and of the binder. The use of binders will attenuate the high activity levels observed for the zeolites and reduce the real production costs. Thus far, all test runs have been conducted on pure zeolite samples.

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APPENDIX "A"

Material balance and product distribution

TABLES 20 - 25
31 - 34

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TABLE 20
STEAM ACTIVATED CATALYST IB1A RUN 10

RAPPORT GAZ DE SYNTHESE							
DATE	12-07-84	12-09-84	12-11-84	12-13-84	12-15-84	12-17-84	12-19-84
CATALYSEUR	IB1A-10-07	IB1A-10-09	IB1A-10-11	IB1A-10-13	IB1A-10-15	IB1A-10-17	IB1A-10-19
ESSAI #	10	10	10	10	10	10	10
# HEURES CUM.	48	97	145	193	241	289	337
POIDS CATALYSEUR (g)	4.70	4.70	4.70	4.70	4.70	4.70	4.70
VOL. CATALYSEUR (ml)	8.00	8.00	8.00	8.00	8.00	8.00	8.00
GHSV (ml/h)/ml	300	300	300	300	300	300	300
PRESSION kPa	1020	1020	1020	1020	1565	1663	1687
T (C)	310	310	310	310	310	310	310
CONVERSION H2 (%wt)	66.93	75.94	76.77	79.10	94.69	85.58	86.29
CONVERSION CO (%wt)	72.47	90.11	94.87	95.62	97.20	95.92	94.17
PRODUITS (%wt)							
HC TOTAL / INPUT	12.15	16.25	17.56	17.93	21.65	19.70	21.28
HC (LIQ) / INPUT	1.50	2.31	2.27	1.83	4.47	3.15	2.98
HC (GAZ) / INPUT	10.65	13.94	15.29	16.10	17.18	16.55	17.40
EAU / INPUT	1.94	5.02	4.74	5.49	4.17	3.54	4.01
CO / INPUT	25.71	9.24	4.79	4.09	2.61	3.81	5.44
CO2 / INPUT	45.31	62.76	66.75	68.73	71.26	67.53	67.78
H2 / INPUT	2.19	1.59	1.54	1.38	1.01	0.95	0.91
BILAN MASSE (%wt)	87.30	94.86	95.37	97.63	100.73	95.53	99.41
SELECTIVITE (% wt)							
C1/HC TOTAUX	34.94	36.09	39.51	41.48	39.76	46.80	47.63
C2/HC TOTAUX	15.48	15.95	16.76	17.70	14.71	14.75	14.10
C3/HC TOTAUX	11.06	11.21	10.85	11.02	9.39	9.68	8.93
C4/HC TOTAUX	17.17	14.30	12.65	12.50	9.90	9.81	7.54
C5+/HC TOTAUX	21.35	22.45	20.23	17.30	26.24	20.95	21.80
P O N A (%wt)							
P / HC (LIQ)	31.53	33.38	36.36	36.33	35.71	34.41	33.79
O / HC (LIQ)	25.89	24.17	25.37	27.39	24.96	25.93	26.77
N / HC (LIQ)	9.83	9.50	8.58	9.20	9.67	10.80	10.72
A / HC (LIQ)	32.74	32.95	29.69	27.08	29.66	28.96	28.72

TABLE 21
IB1A RUN 12

RAPPORT GAZ DE SYNTHESE

DATE	28-01-85	30-01-85	01-02-85	03-02-85	05-02-85	08-02-85
CATALYSEUR	IB1A-12-28	IB1A-12-30	IB1A-12-01	IB1A-12-03	IB1A-12-05	IB1A-12-08
ESSAI #	12	12	12	12	12	12
# HEURES CUM.	48	96	144	192	240	312
POIDS CATALYSEUR (g)	5.45	5.45	5.45	5.45	5.45	5.45
VOL. CATALYSEUR (ml)	8.00	8.00	8.00	8.00	8.00	8.00
SHSV (ml/h)/ml	300	300	300	300	300	300
PRESSION kPa	1020	1020	1020	1020	1020	1020
T1 (°C)	310	310	310	310	310	310
CONVERSION H2 (%wt)	67.75	72.96	75.83	77.29	78.32	74.55
CONVERSION CO (%wt)	83.84	90.57	95.57	88.61	90.14	85.22
PRODUITS (%wt)						
HC TOTAL / INPUT	11.58	14.49	16.40	16.60	17.18	16.61
HC (LIQ) / INPUT	1.82	3.03	3.69	2.92	2.92	3.02
HC (GAZ) / INPUT	9.76	11.46	12.71	13.68	14.26	13.58
EAU / INPUT	2.76	5.05	4.81	3.78	3.83	5.13
CO / INPUT	33.75	18.13	13.47	10.63	9.20	13.79
CO2 / INPUT	32.06	44.22	49.32	51.59	53.16	50.23
H2 / INPUT	2.42	1.81	1.61	1.52	1.45	1.70
BILAN MASSE (%wt)	82.57	83.70	85.62	84.12	84.83	87.46
SELECTIVITE (% wt)						
C1/HC TOTAUX	34.71	36.09	37.26	40.57	41.57	38.94
C2/HC TOTAUX	14.12	15.06	14.88	15.79	15.99	15.86
C3/HC TOTAUX	10.51	8.06	8.31	9.68	9.65	10.45
C4/HC TOTAUX	16.82	13.50	11.58	11.15	10.83	11.43
C5+/HC TOTAUX	23.84	27.29	27.98	22.80	21.96	23.32
P O N A (%wt)						
P / HC (LIQ)	27.19	28.34	28.54	28.23	26.48	30.57
O / HC (LIQ)	27.52	25.43	26.89	21.53	25.34	29.54
N / HC (LIQ)	11.53	10.02	10.32	10.64	10.48	11.35
A / HC (LIQ)	33.77	36.22	34.24	39.61	37.69	28.53

TABLE 22
IB2A RUN 11

RAPPORT GAZ DE SYNTHESE					
DATE	1-28-85	1-30-85	2-01-85	2-03-85	2-05-85
CATALYSEUR	IB2A-11-28	IB2A-11-30	IB2A-11-01	IB2A-11-03	IB2A-11-05
ESSAI #	11	11	11	11	11
# HEURES CUM.	48	96	144	192	240
POIDS CATALYSEUR (g)	5.10	5.10	5.10	5.10	5.10
VOL. CATALYSEUR (ml)	8.00	8.00	8.00	8.00	8.00
SHSV (nl/h)/ml	300	300	300	300	300
PRESSION kPa	1050	1050	1050	1156	1276
T1 (°C)	310	310	310	310	310
CONVERSION H2 (%wt)	74.66	79.56	83.26	81.40	82.11
CONVERSION CO (%wt)	80.72	90.29	92.14	92.96	93.79
PRODUITS (%wt)					
HC TOTAL / INPUT	15.34	18.20	19.06	18.23	19.04
HC (LIQ) / INPUT	3.09	4.12	3.97	3.84	3.30
HC (GAZ) / INPUT	12.26	14.09	15.09	15.49	15.74
EAU / INPUT	2.92	3.88	3.78	3.07	4.05
CO / INPUT	19.02	9.09	7.35	6.58	5.81
CO2 / INPUT	50.76	59.98	61.98	62.29	62.40
H2 / INPUT	1.65	1.33	1.09	1.21	1.17
BILAN MASSE (%wt)	98.79	92.46	93.26	92.48	92.46
SELECTIVITE:(%wt)					
C1/HC TOTAUX	28.83	32.51	34.74	36.63	39.54
C2/HC TOTAUX	14.72	15.15	15.44	15.47	15.75
C3/HC TOTAUX	11.20	9.84	9.51	10.30	10.21
C4/HC TOTAUX	15.81	13.24	12.54	11.38	11.03
C5+/HC TOTAUX	29.43	30.26	27.77	26.23	23.47
P O N A (%wt)					
P / HC (LIQ)	32.43	31.50	32.46	27.61	26.89
O / HC (LIQ)	24.32	25.35	24.13	23.29	23.01
N / HC (LIQ)	11.21	11.15	9.89	10.05	10.90
A / HC (LIQ)	32.04	31.99	33.51	39.05	39.19

TABLE 23
IBJA RUN 15

RAPPORT GAZ DE SYNTHESE

DATE	3-10-85	3-12-85	3-14-85	3-16-85	3-18-85	3-20-85	3-22-85
CATALYSEUR	IBJA-15-10	IBJA-15-12	IBJA-15-14	IBJA-15-16	IBJA-15-18	IBJA-15-20	IBJA-15-22
ESSAI #	15	15	15	15	15	15	15
# HEURES CUM.	48	96	144	192	240	288	336
POIDS CATALYSEUR (g)	4.76	4.76	4.76	4.76	4.76	4.76	4.76
VOL. CATALYSEUR (ml)	8.00	8.00	8.00	8.00	8.00	8.00	8.00
GHSV (ml/h)/ml	298	298	298	298	298	298	298
PRESSION kPa	1020	1020	1020	1020	1020	1020	1701
T1 (°C)	310	310	310	310	310	310	310
CONVERSION H2 (%wt)	59.39	62.61	67.40	67.84	66.49	65.08	73.61
CONVERSION CO (%wt)	58.32	64.94	65.52	65.70	68.23	66.21	74.57
PRODUITS (%wt)							
HC TOTAL / INPUT	12.58	14.47	15.23	15.29	15.05	14.73	15.77
HC (LIQ) / INPUT	1.59	2.98	2.90	2.66	2.72	2.29	2.27
HC (GAZ) / INPUT	10.99	11.49	12.34	12.62	12.33	12.45	13.51
EAU / INPUT	3.75	6.39	7.50	6.55	6.67	5.80	6.55
CO / INPUT	38.78	32.71	32.08	31.93	29.59	31.48	23.69
CO2 / INPUT	36.57	39.93	41.63	39.76	41.46	41.95	43.96
HC / INPUT	2.89	2.51	2.55	2.51	2.30	2.39	1.80
BILAN MASSE (%wt)	94.58	96.01	98.99	96.03	95.08	96.36	91.77
SELECTIVITE:(% wt)							
C1/HC TOTAUX	34.00	31.70	34.61	37.26	38.19	39.27	43.77
C2/HC TOTAUX	17.05	15.36	16.30	16.78	16.64	17.49	17.38
C3/HC TOTAUX	12.20	11.28	11.05	10.79	10.41	10.92	10.53
C4/HC TOTAUX	16.51	14.56	13.61	12.73	12.11	12.37	10.08
C5+/HC TOTAUX	20.25	27.10	24.43	22.44	22.66	19.94	18.24
P O N A (%wt)							
P / HC (LIQ)	24.70	26.59	27.45	26.47	24.94	23.61	25.63
O / HC (LIQ)	23.10	25.84	28.42	30.69	30.12	27.94	26.72
N / HC (LIQ)	15.02	13.99	13.69	13.40	13.49	13.47	12.79
A / HC (LIQ)	37.19	33.59	30.44	29.44	31.45	34.99	34.86

TABLE 24
IB4A RUN 16

RAPPORT GAZ DE SYNTHESE							
DATE	3-10-85	3-12-85	3-14-85	3-16-85	3-18-85	3-20-85	3-22-85
CATALYSEUR	IB4A-16-10	IB4A-16-12	IB4A-16-14	IB4A-16-16	IB4A-16-18	IB4A-16-20	IB4A-16-22
ESSAI #	16	16	16	16	16	16	16
# HEURES CUM.	48	96	144	192	240	288	336
POIDS CATALYSEUR (g)	5.28	5.28	5.28	5.28	5.28	5.28	5.28
VOL. CATALYSEUR (ml)	8.00	8.00	8.00	8.00	8.00	8.00	8.00
GHSV (ml/h)/ml	302	302	302	302	302	302	302
PRESSION kPa	1020	1020	1020	1020	1020	1020	1020
T1 (°C)	310	310	310	310	310	310	310
CONVERSION H2 (%wt)	56.97	58.04	58.30	59.25	67.88	63.54	66.83
CONVERSION CO (%wt)	46.67	52.14	56.51	63.10	69.51	66.57	70.34
PRODUITS (%wt)							
HC TOTAL / INPUT	9.20	10.60	12.46	14.29	11.22	13.70	17.33
HC (LIQ) / INPUT	0.97	1.71	2.55	3.42	2.57	3.45	4.24
HC (GAZ) / INPUT	8.24	8.89	9.91	10.87	8.65	10.25	13.09
EAU / INPUT	4.60	7.59	8.18	6.34	6.86	7.66	6.79
CO / INPUT	49.65	44.60	40.51	34.33	28.43	31.19	27.67
CO2 / INPUT	23.53	28.01	34.46	38.59	33.46	40.60	49.73
H2 / INPUT	2.98	2.86	2.86	2.85	2.17	2.45	2.23
BILAN MASSE (%wt)	89.97	93.66	95.47	96.88	82.14	95.59	103.95
SELECTIVITE:(% wt)							
C1/HC TOTAUX	31.23	29.66	28.09	26.62	27.04	26.13	26.12
C2/HC TOTAUX	14.84	13.96	13.24	12.68	13.16	12.78	12.63
C3/HC TOTAUX	16.39	17.28	17.04	16.26	17.29	16.97	16.61
C4/HC TOTAUX	22.70	19.49	17.80	15.46	16.24	15.70	14.73
C5+/HC TOTAUX	14.85	19.61	23.84	28.98	26.28	28.42	28.91
P O N A (%wt)							
P / HC (LIQ)	45.45	54.41	56.76	55.41	59.62	54.70	55.73
O / HC (LIQ)	28.04	26.52	25.55	29.88	21.54	29.51	27.00
N / HC (LIQ)	11.38	8.33	7.94	6.81	9.22	7.38	8.73
A / HC (LIQ)	15.13	10.75	9.75	7.90	9.62	8.41	8.55

TABLE 25
IB1B RUN 18

RAPPORT GAZ DE SYNTHESE

DATE	4-29-85	05-01-85	05-03-85	05-05-85	05-07-85	5-08-85
CATALYSEUR	IB1B-18-29	IB1B-19-01	IB1B-18-03	IB1B-18-05	IB1B-18-07	IB1B-18-08
ESSAI #	18	18	18	18	18	18
# HEURES CUM.	48	96	144	192	240	265
POIDS CATALYSEUR (g)	5.65	5.65	5.65	5.65	5.65	5.65
VOL. CATALYSEUR (ml)	8.00	8.00	8.00	8.00	8.00	8.00
GHSV (ml/h/ml	300	300	300	300	300	300
PRESSION kPa	1020	1020	1020	1020	1020	1020
T1 (°C)	310	310	310	310	310	310
CONVERSION H2 (%wt)	30.76	49.46	51.49	50.03	49.81	48.33
CONVERSION CO (%wt)	18.25	34.10	36.70	35.07	34.09	34.17
PRODUITS (%wt)						
HC TOTAL / INPUT	5.20	8.04	8.47	9.38	7.68	7.80
HC (LIQ) / INPUT	0.00	0.59	0.50	0.41	0.21	0.13
HC (GAZ) / INPUT	5.20	7.44	7.97	7.97	7.48	7.67
EAU / INPUT	1.59	9.90	8.93	7.67	7.27	9.71
CO / INPUT	76.44	61.55	59.14	60.64	61.58	61.49
CO2 / INPUT	5.42	12.47	13.84	13.76	12.90	12.15
H2 / INPUT	4.52	3.34	3.18	3.30	3.36	3.41
BILAN MASSE (%wt)	93.16	94.29	93.57	93.76	92.50	94.55
SELECTIVITE:(% wt)						
C1/HC TOTAUX	29.85	28.91	32.07	37.12	42.29	43.54
C2/HC TOTAUX	12.13	12.61	13.56	17.74	15.66	18.10
C3/HC TOTAUX	11.70	13.67	15.14	16.93	19.41	17.76
C4/HC TOTAUX	27.40	24.02	22.36	19.24	18.49	16.90
C5+/HC TOTAUX	18.92	20.80	16.87	8.97	5.15	3.71
P O N A (%wt)						
P / HC (LIQ)	0.00	26.29	29.14	30.09	0.00	0.00
O / HC (LIQ)	0.00	30.05	28.14	23.65	0.00	0.00
N / HC (LIQ)	0.00	14.78	14.55	15.19	0.00	0.00
A / HC (LIQ)	0.00	28.29	28.17	31.07	0.00	0.00

TABLE 31
Ni-IB2A RUN 19
(Ni EXCHANGED)

RAPPORT GAZ DE SYNTHESE					
DATE	15-07-85	17-07-85	19-07-85	21-07-85	23-07-85
CATALYSEUR	Ni-IB-19-15	Ni-IB-19-17	Ni-IB-19-19	Ni-IB-19-21	Ni-IB-19-23
ESSAI #	19	19	19	19	19
# HEURES CUM.	48	96	144	192	240
POIDS CATALYSEUR (g)	4.99	4.99	4.99	4.99	4.99
VOL. CATALYSEUR (ml)	8.00	8.00	8.00	8.00	8.00
SHSV (ml/h)/ml	345	345	390	390	390
PRESSION kPa	1102	1089	1123	1144	1233
T1 (°C)	310	310	310	310	310
CONVERSION H2 (%wt)	74.83	77.71	79.76	80.14	80.36
CONVERSION CO (%wt)	95.67	96.11	96.12	96.93	96.98
PRODUITS (%wt)					
HC TOTAL / INPUT	19.22	19.69	18.26	19.05	19.04
HC (LIQ) / INPUT	0.61	0.92	2.08	1.97	1.72
HC (GAZ) / INPUT	18.61	18.77	16.19	17.09	17.32
EAU / INPUT	6.43	6.70	4.62	4.32	4.47
CO / INPUT	3.96	1.72	3.61	2.85	2.80
CO2 / INPUT	55.70	56.40	59.54	61.90	62.49
H2 / INPUT	2.15	1.92	1.40	1.40	1.43
BILAN MASSE (% wt)	87.45	86.43	87.42	89.22	90.23
SELECTIVITE (% wt)					
C1/HC TOTAUX	47.04	47.72	48.90	46.07	47.91
C2/HC TOTAUX	23.30	23.53	21.90	21.90	22.14
C3/HC TOTAUX	1.30	1.50	1.40	1.41	1.41
C4/HC TOTAUX	14.75	14.31	13.72	12.77	12.46
C5+/HC TOTAUX	13.61	12.94	19.19	17.84	16.09
P O N A (%wt)					
P / HC (LIQ)	29.15	27.50	27.27	25.90	23.37
O / HC (LIQ)	4.78	4.29	5.74	6.22	5.79
N / HC (LIQ)	18.45	16.54	15.13	14.15	12.88
A / HC (LIQ)	47.62	51.67	51.87	53.74	57.96

TABLE 32
Co-IB2A RUN 20
(Co EXCHANGED)

RAPPORT GAZ DE SYNTHESE					
DATE	15-07-85	17-07-85	19-07-85	21-07-85	23-07-85
CATALYSEUR	Co-IB-20-15	Co-IB-20-17	Co-IB-20-19	Co-IB-20-21	Co-IB-20-23
ESSAI #	20	20	20	20	20
# HEURES CUM.	48	96	144	192	240
POIDS CATALYSEUR (g)	4.93	4.93	4.93	4.93	4.93
VOL. CATALYSEUR (ml)	8.00	8.00	8.00	8.00	8.00
GHSV (ml/h)/ml	428	428	454	454	454
PRESSION kPa	1316	1385	1488	1550	1633
T1 (°C)	310	310	310	310	310
CONVERSION H2 (%wt)	78.48	78.23	78.23	77.06	74.55
CONVERSION CO (%wt)	97.84	98.17	97.58	97.23	96.68
PRODUITS (%wt)					
HC TOTAL / INPUT	18.71	19.43	18.49	18.24	17.26
HC (LIQ) / INPUT	3.07	3.65	4.82	5.35	5.01
HC (GAZ) / INPUT	15.64	15.78	13.66	12.89	12.84
EAU / INPUT	5.80	7.46	5.69	5.71	5.78
CO / INPUT	1.99	1.69	2.25	2.57	3.07
CO2 / INPUT	58.79	60.15	60.13	60.26	56.92
H2 / INPUT	1.66	1.68	1.50	1.61	1.85
BILAN MASSE (% wt)	86.94	90.42	88.06	88.40	85.48
SELECTIVITE (% wt)					
C1/HC TOTAUX	36.45	35.26	31.23	29.28	29.07
C2/HC TOTAUX	17.79	16.36	14.25	13.67	13.92
C3/HC TOTAUX	1.76	3.82	1.86	2.07	2.19
C4/HC TOTAUX	17.55	16.03	16.09	15.86	16.10
C5+/HC TOTAUX	26.45	28.53	36.58	39.13	38.72
P O N A (%wt)					
P / HC (LIQ)	37.37	40.50	41.68	41.45	41.17
O / HC (LIQ)	12.16	12.76	16.58	19.82	22.77
N / HC (LIQ)	16.69	15.09	13.40	12.76	12.66
A / HC (LIQ)	33.78	31.65	28.35	25.97	23.39

TABLE 33
La-IB2A-Co RUN 23
(La EXCHANGED AND Co IMPREGNATED)

RAPPORT GAZ DE SYNTHESE						
DATE	04-08-85	06-08-85	08-08-85	10-08-85	12-08-85	14-08-85
CATALYSEUR	Co-IB-23-04	Co-IB-23-06	Co-IB-23-08	Co-IB-23-10	Co-IB-23-12	Co-IB-23-14
ESSAI #	23*	23	23	23	23	23
# HEURES CUM.	48	96	144	192	240	288
POIDS CATALYSEUR (g)	5.45	5.45	5.45	5.45	5.45	5.45
VOL. CATALYSEUR (ml)	8.00	8.00	8.00	8.00	8.00	8.00
GHSV (ml/h)/ml	300	300	300	300	300	300
PRESSION kPa	1020	1020	1020	1020	1020	1972
T1 (°C)	300	300	300	300	310	310
CONVERSION H2 (%wt)	90.06	83.40	83.40	83.99	86.77	91.29
CONVERSION CO (%wt)	84.65	96.41	97.06	97.25	98.02	98.92
PRODUITS (%wt)						
HC TOTAL / INPUT	16.53	18.58	18.47	19.05	19.85	20.21
HC (LIQ) / INPUT	0.92	2.05	1.83	2.03	1.69	1.77
HC (GAZ) / INPUT	15.61	16.53	16.64	17.03	18.15	18.44
EAU / INPUT	3.36	4.19	4.04	5.03	4.91	4.52
CO / INPUT	14.31	3.35	2.74	2.56	1.84	1.01
CO2 / INPUT	52.92	63.20	63.00	64.39	64.74	63.39
H2 / INPUT	1.35	1.11	1.11	1.09	0.90	0.59
BILAN MASSE (% wt)	88.47	90.44	89.35	92.13	92.24	89.72
SELECTIVITE (% wt)						
C1/HC TOTAUX	58.96	51.96	52.35	52.04	54.78	54.96
C2/HC TOTAUX	15.50	16.18	17.22	17.57	18.31	18.46
C3/HC TOTAUX	2.61	2.11	2.15	2.14	2.17	1.64
C4/HC TOTAUX	12.40	12.93	12.77	12.34	11.51	11.04
C5+/HC TOTAUX	10.54	16.83	15.51	15.92	13.24	13.91
P O N A (%wt)						
P / HC (LIQ)	29.71	32.88	33.73	33.23	30.48	33.71
O / HC (LIQ)	24.78	25.93	26.13	25.48	24.64	22.47
N / HC (LIQ)	12.14	13.01	13.05	13.17	13.43	13.13
A / HC (LIQ)	33.37	28.18	27.09	28.12	31.45	30.70

TABLE 34
IB2A(Co+La) RUN 24
(Co AND La IMPRESNATED)

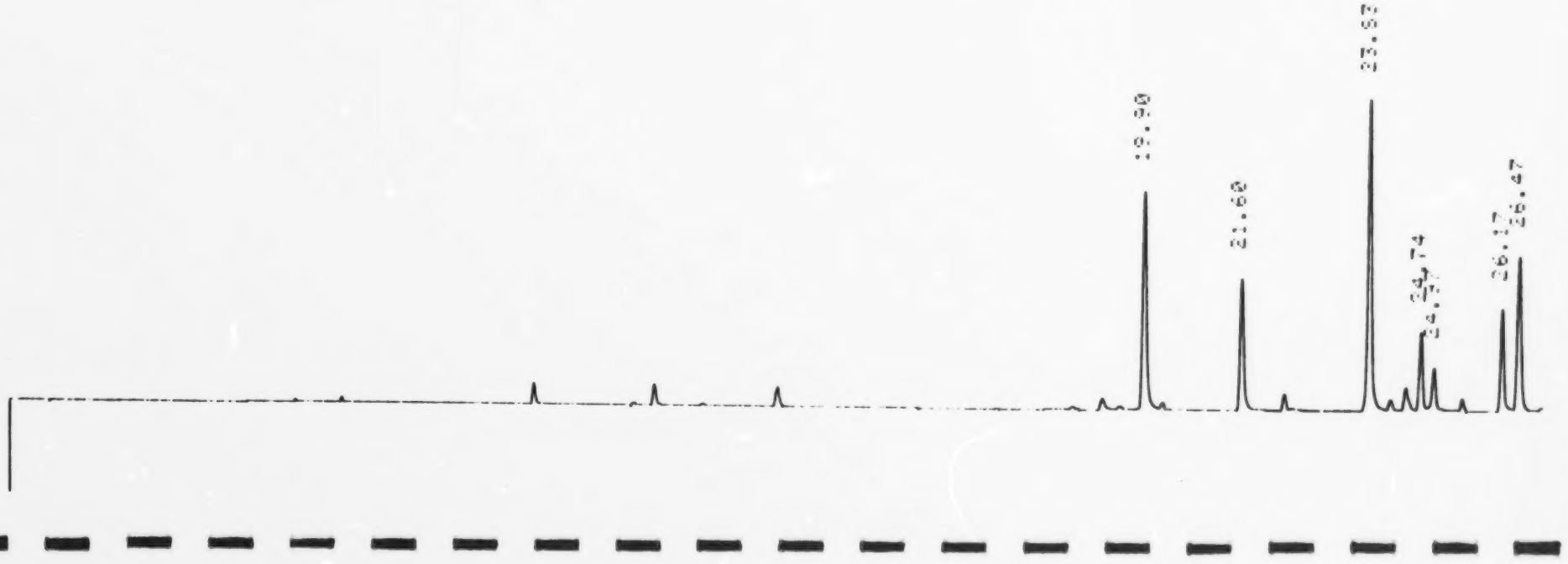
RAPPORT GAZ DE SYNTHESE						
DATE	04-08-85	06-08-85	08-08-85	10-08-85	12-08-85	14-08-85
CATALYSEUR	La-IB-24-04	La-IB-24-06	La-IB-24-08	La-IB-24-10	La-IB-24-12	La-IB-24-14
ESSAI #	24	24	24	24	24	24
# HEURES CUM.	48	96	144	192	240	288
POIDS CATALYSEUR (g)	5.91	5.91	5.91	5.91	5.91	5.91
VOL. CATALYSEUR (ml)	8.00	8.00	8.00	8.00	8.00	8.00
GHSV (ml/h)/ml	300	300	300	300	300	300
PRESSION kPa	1020	1020	1020	1020	1020	1700
T1 (°C)	300	300	300	300	310	310
CONVERSION H2 (%wt)	73.76	78.21	78.69	78.67	81.75	85.96
CONVERSION CO (%wt)	76.46	87.36	88.74	90.47	96.98	97.91
PRODUITS (%wt)						
HC TOTAL / INPUT	11.40	14.16	15.47	15.40	17.02	17.00
HC (LIQ) / INPUT	1.91	3.68	4.89	4.73	4.90	6.22
HC (GAZ) / INPUT	9.49	10.49	10.58	10.67	12.11	10.79
EAU / INPUT	2.35	4.65	4.37	4.65	3.96	6.57
CO / INPUT	22.16	11.96	10.55	8.94	2.83	1.96
CO2 / INPUT	45.45	55.30	57.40	58.65	63.53	61.10
H2 / INPUT	1.53	1.34	1.33	1.32	1.14	0.97
BILAN MASSE (% wt)	82.89	87.31	89.12	88.97	88.47	87.50
SELECTIVITE (% wt)						
C1/HC TOTAUX	39.97	33.49	30.96	31.12	31.09	28.27
C2/HC TOTAUX	13.66	11.92	11.26	11.66	12.07	11.84
C3/HC TOTAUX	4.61	3.87	3.61	3.63	3.33	2.62
C4/HC TOTAUX	19.06	18.42	17.01	17.11	17.69	14.94
C5+/HC TOTAUX	22.70	32.30	37.17	36.48	35.83	42.34
P O N A (%wt)						
P / HC (LIQ)	42.83	47.03	50.27	50.48	51.02	48.90
O / HC (LIQ)	32.52	37.23	34.59	34.77	34.65	36.00
N / HC (LIQ)	10.93	7.64	7.24	7.31	7.65	7.63
A / HC (LIQ)	13.72	8.10	7.89	7.44	6.67	7.47

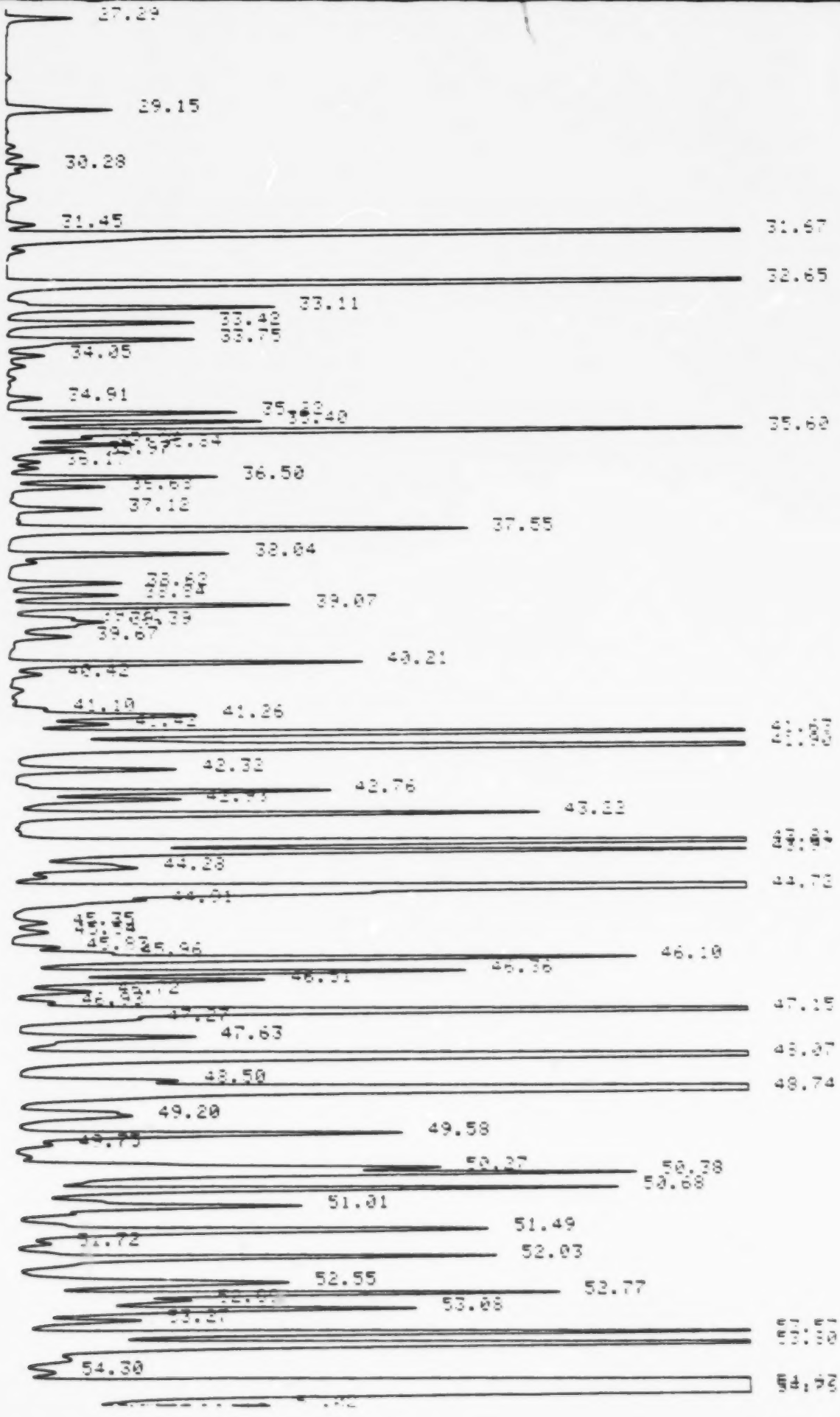
APPENDIX "B"

Gas chromatograms of gasoline collected
from catalysts IB2A, IB4A and
IB2A+(La+Co)

CRIQ

IB2A RUN 11

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36.50
37.12
37.55
38.04
39.07
39.67
40.21
40.42
41.10
41.26
42.32
42.76
43.33
44.28
44.73
45.96
46.10
46.36
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48.50
48.74
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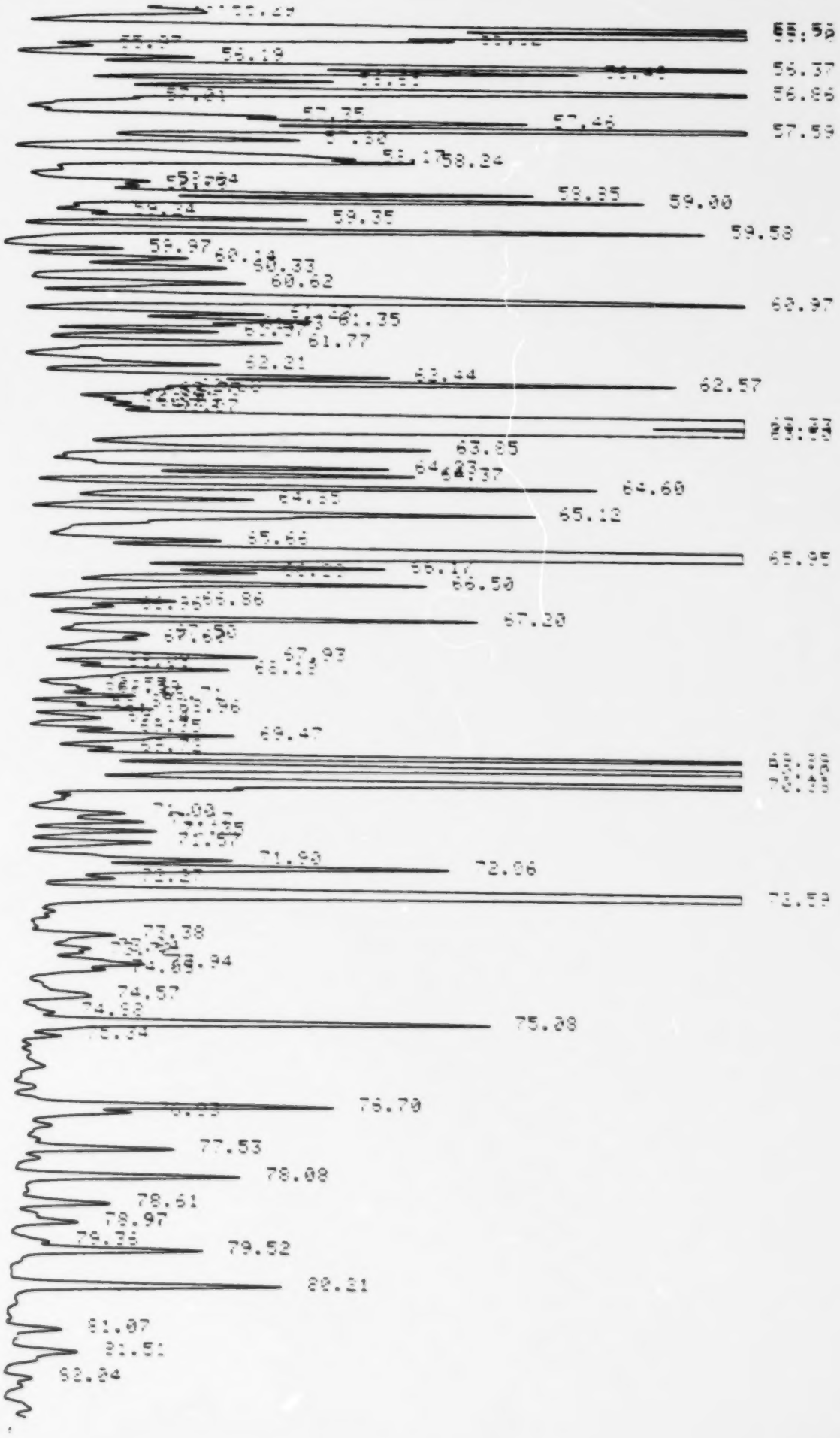
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65.95
66.50
67.20
67.97
69.47
72.06
73.38
74.57
75.38
76.79
77.53
78.08
78.61
78.97
79.52
80.21
81.07
81.51
82.04

85.67
87.10
88.75
92.42

OVEN TEMP NOT READY

4.17

6.20

6.70

13.53

RUN TIME = 22.18 MIN

22.37

23.86

24.34

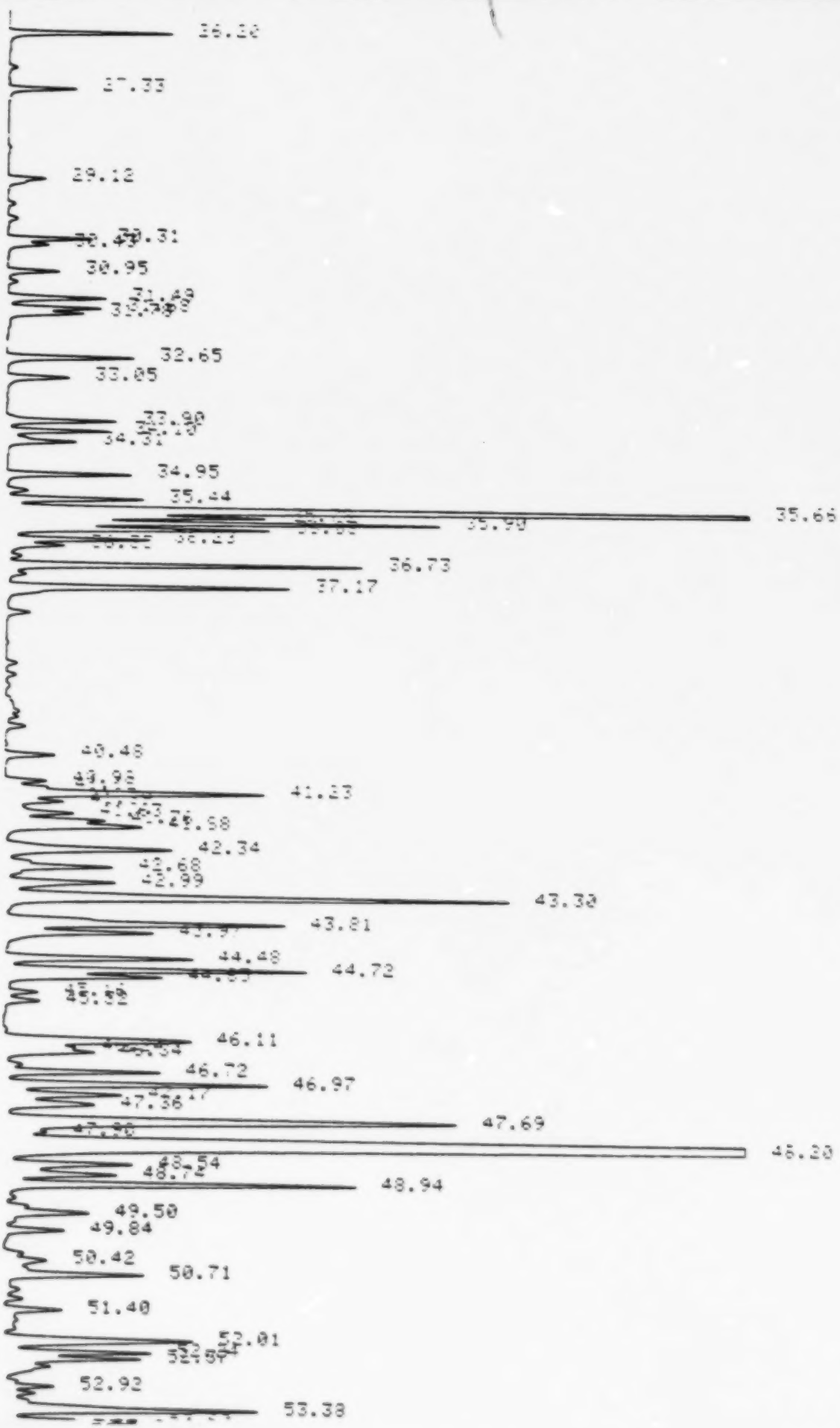
24.50

24.77

25.00

25.50

IB4A RUN 16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41.23
42.34
43.30
43.81
44.48
44.72
46.11
46.72
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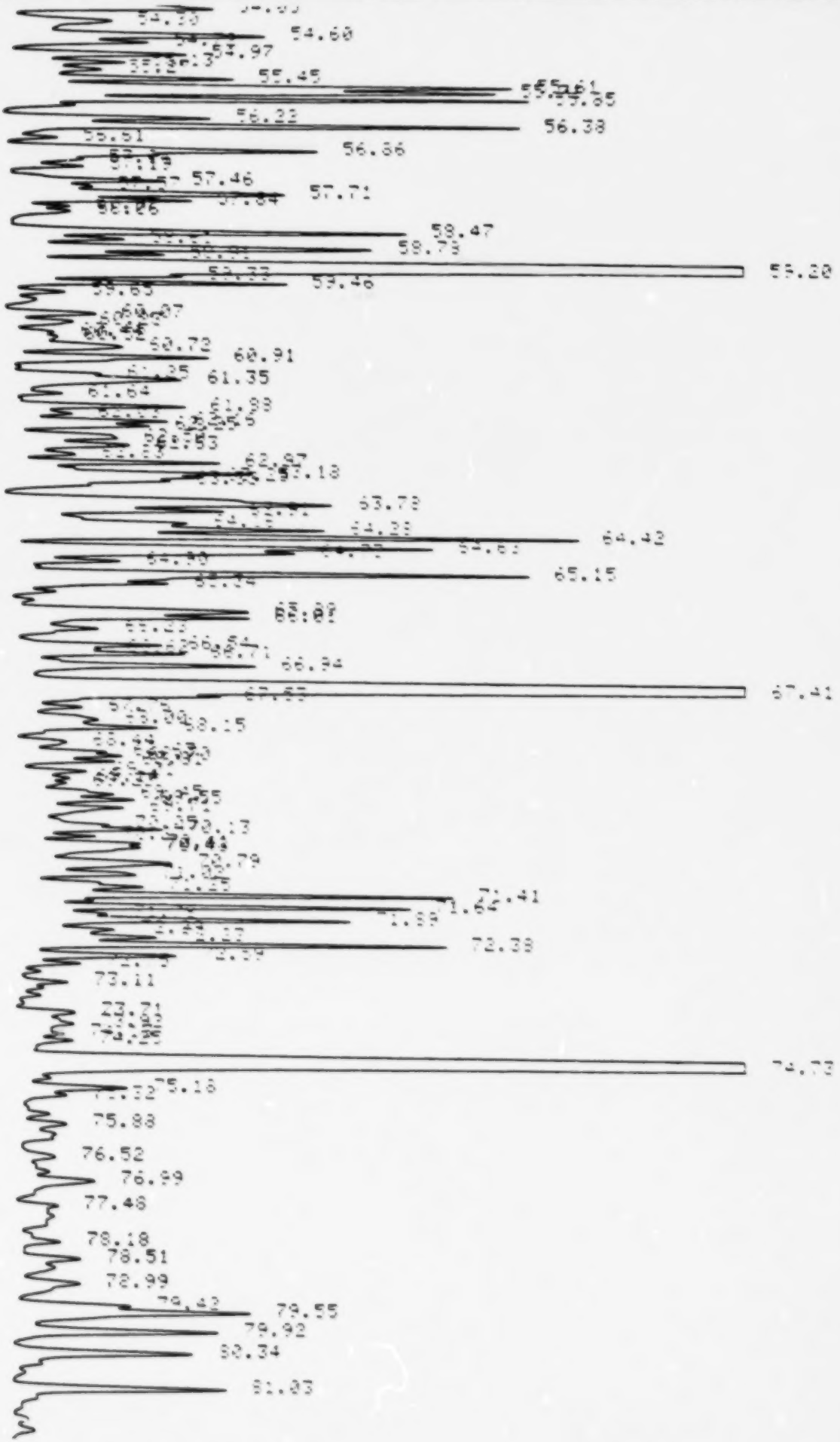
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78.99
79.55
79.92
80.34
81.03

83.38
84.39
C12
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91.06
92.77
93.63
93.16
C13
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106.25
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107.23
C14
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113.26
114.65
C15
115.79
117.35
118.33
C16
119.75
120.51
121.33
C17
121.45
123.87
C18
124.78
125.45
126.07
C19
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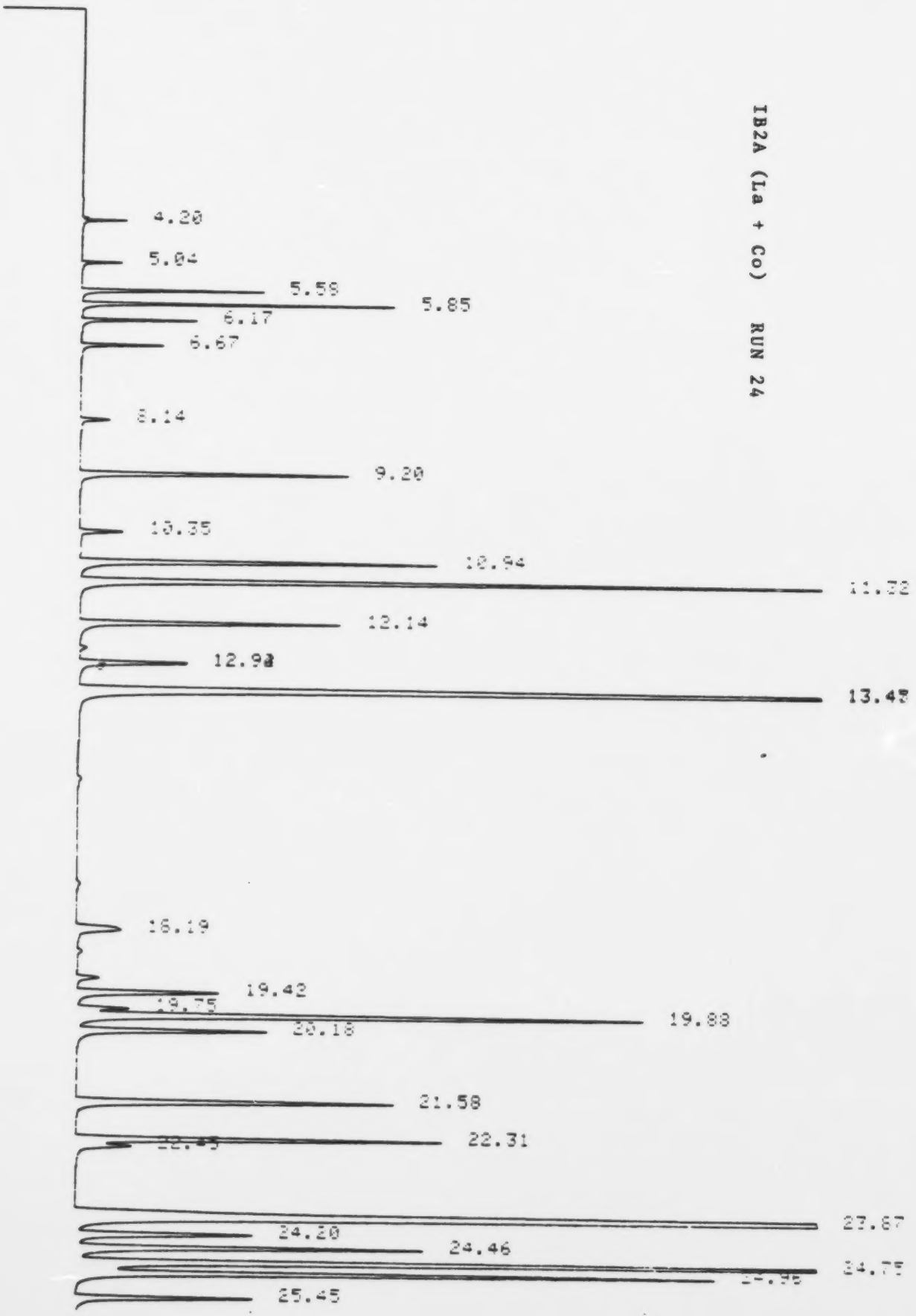
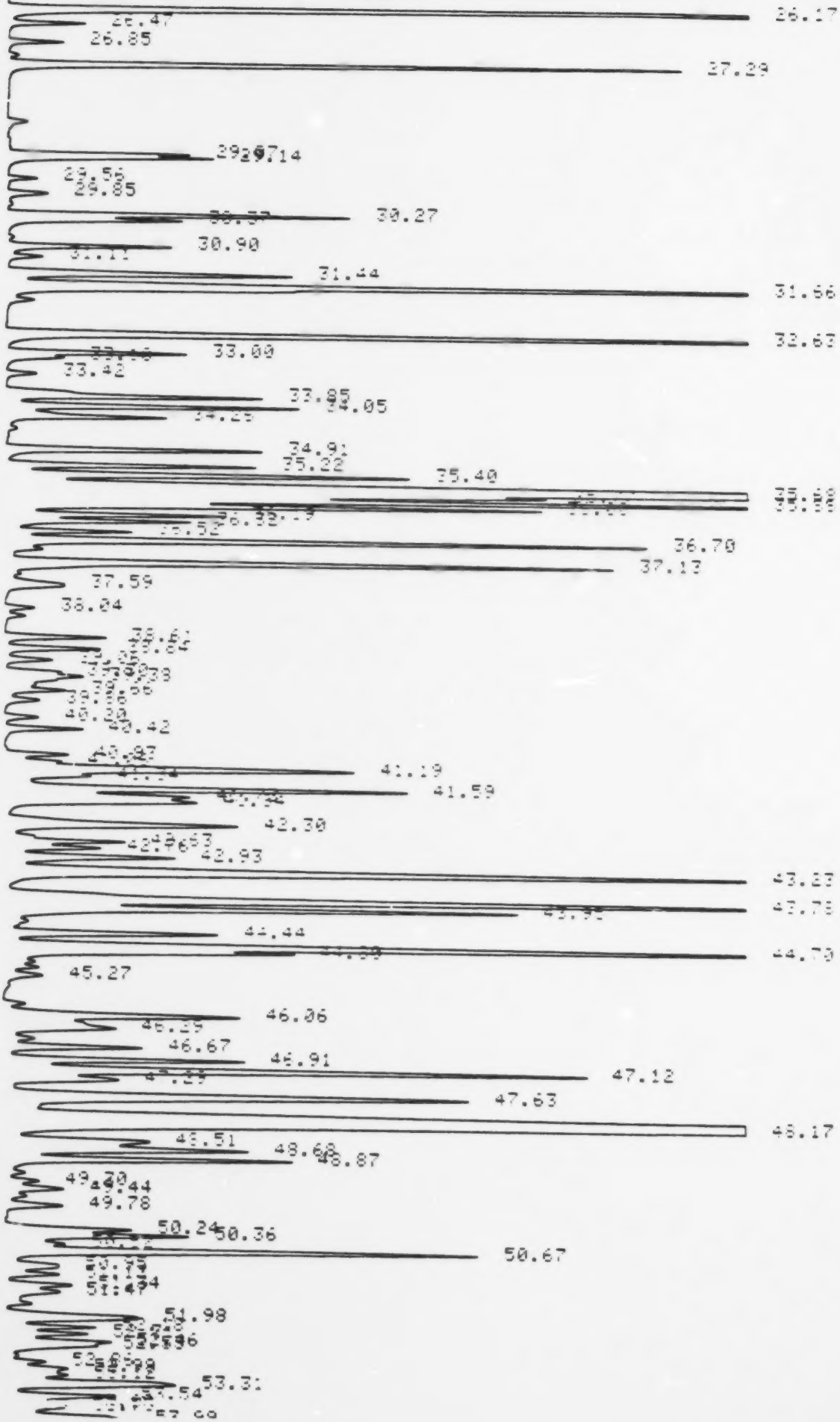
126.97
127.67
128.26
C20
129.15
RUN

OVEN TEMP NOT READY

IB2A (La + Co) RUN 24

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34.05
34.91
35.22
35.40
36.70
37.13
37.59
38.04
41.19
41.59
42.30
42.93
43.37
43.78
44.44
44.79
45.27
46.06
46.67
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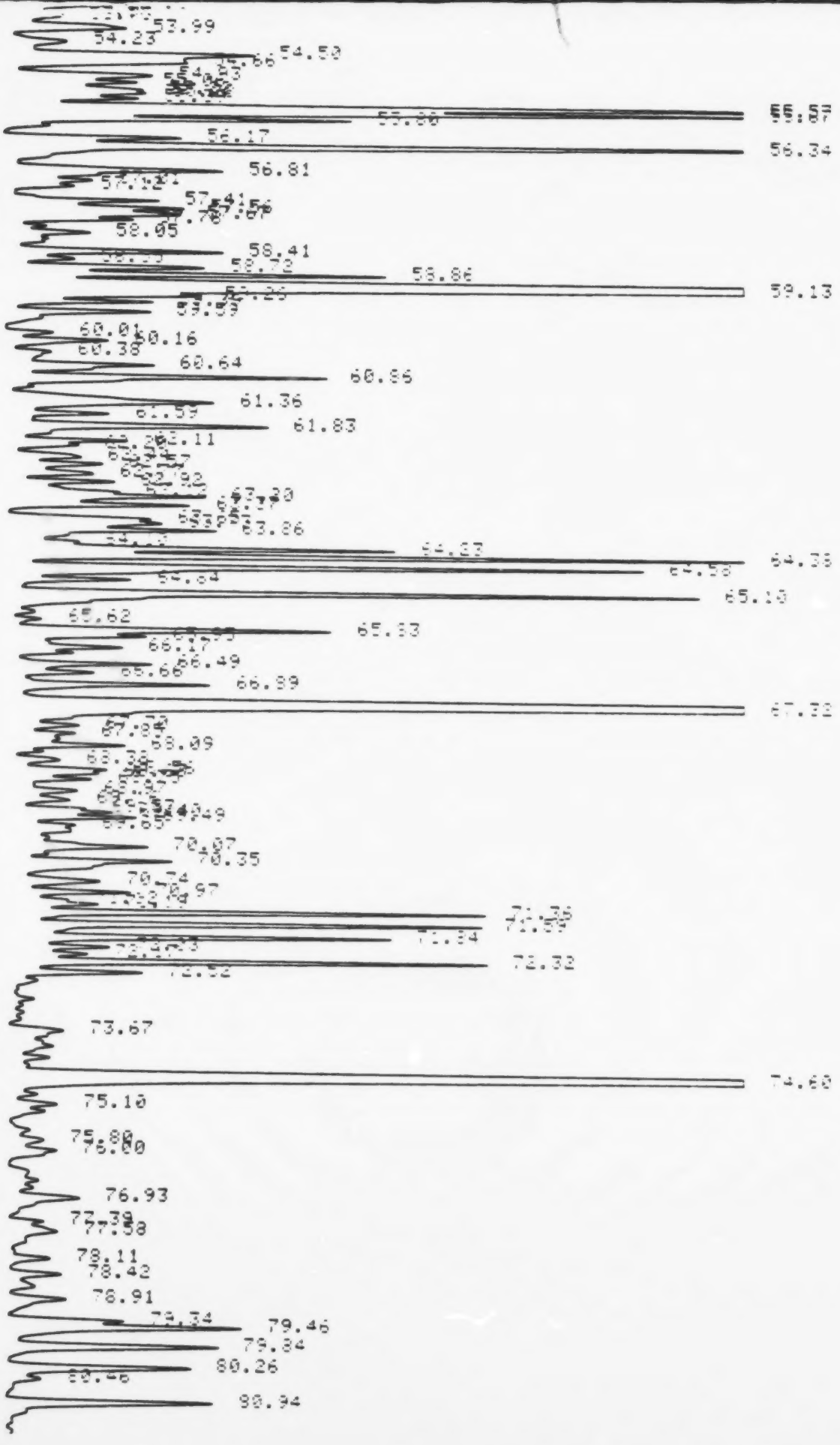
53.31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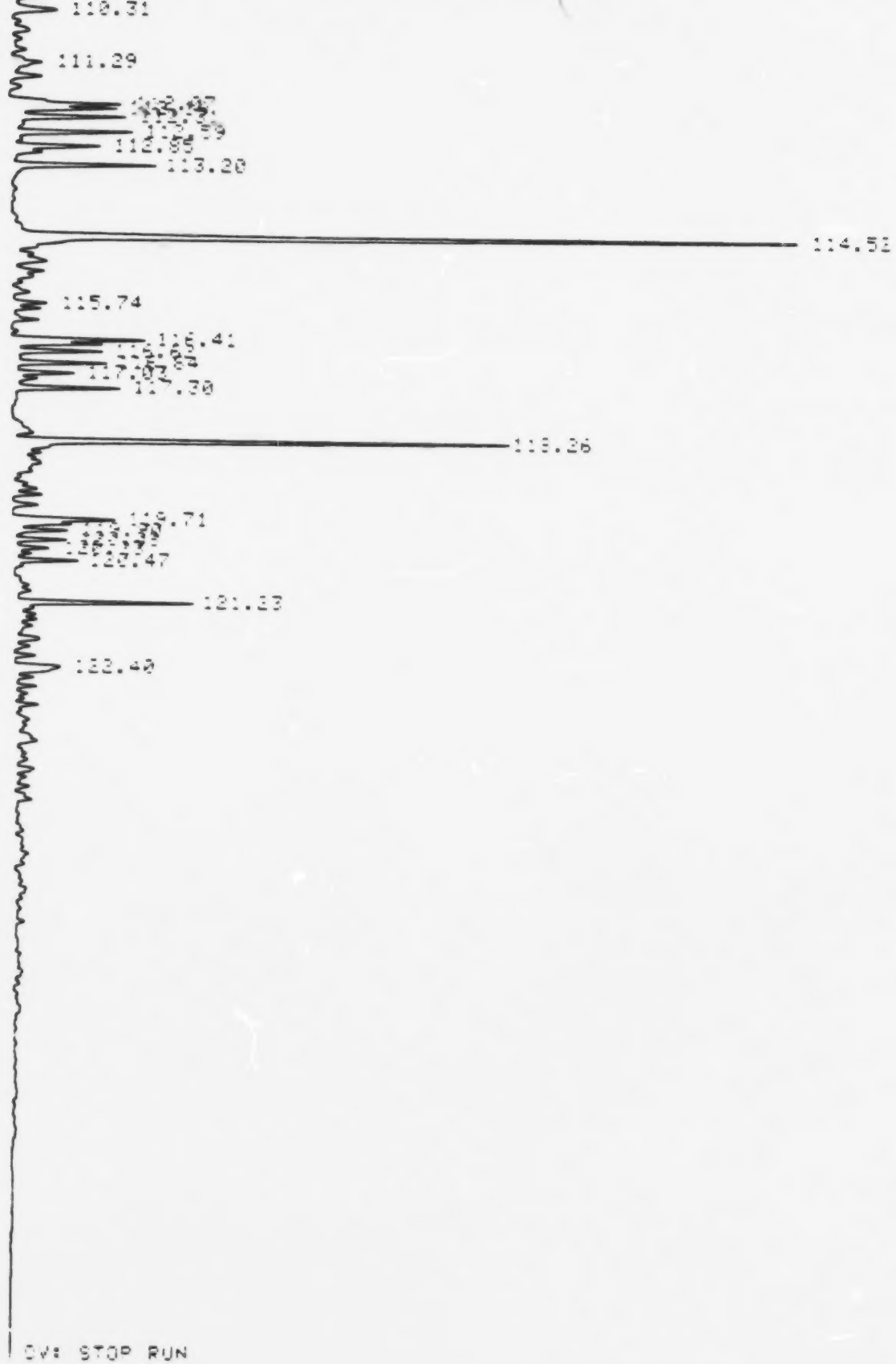
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122.40
CV: STOP RUN

APPENDIX "C"

Report from Professor B. Wojciechowski

CRIQ

Testing of Synthesis Catalysts Supplied by the Centre de Recherche Industrielle du Quebec

B.W. Wojciechowski

Chemical Engineering Department
Queen's University at Kingston, Ontario

January 1986

ABSTRACT

Three versions of catalyst 2A were tested for extended periods at specified synthesis conditions. It was found that under the specified conditions the catalysts convert carbon monoxide to hydrocarbons and carbon dioxide in about equimolar amounts.

The hydrocarbons formed are mostly confined to the boiling range of gasoline and below. In the hydrocarbon product, gasoline selectivity up to 65 % by weight was observed but not at standard operating conditions where 25 % gasoline selectivity was the best achieved. The gasoline produced is high in isomers, olefins and aromatics. At the end of each run the catalyst was found to be heavily coated with carbon, leading to the suspicion that these tests do not reveal the catalyst in the best light possible. It is suggested that the catalyst be evaluated at more hydrogen rich feed ratios to ascertain whether such a change in operating conditions will reduce carbon deposition and CO_2 formation as well as improving selectivity for liquid hydrocarbons.

INTRODUCTION

On September 30, 1985 Pierre Désilets of CRIQ requested by letter that two catalysts supplied in powder form, 2A(1) and 2A(2), be tested for synthesis performance for four weeks each at the following conditions:

Pretreatment

H_2/CO ratio 1:1

GHSV 600 hr^{-1}

Temp. 3 °C/min. to 350 °C and hold for 40 hr.

Pressure 15 psi

Reaction

H_2/CO ratio 1:1

GHSV 300 hr^{-1}

Temp. 350 °C

Pressure 150 psi

It became clear soon after the start of the run that catalyst 2A(1), which was the first to be put on stream, was of low reactivity. Consultation with Kee Leen of CRIQ revealed that the catalyst may have been damaged in preparation. As a consequence 2A(1) was tested for two weeks only. Catalyst

2A(2) was not tested.

Two new batches of catalyst, identified as 2A-(1) and 2A-(2) were supplied in pelletized form by Ben Chang of CRIQ. Each of these was run for three weeks. The first two weeks were spent in pretreatment and operation at the standard conditions specified above while the last week, on request of Ben Chang, was spent operating at 250 psig with other parameters remaining as above.

RESULTS

A summary of the results is shown in tables 1-3. Run sheets have been submitted separately together with samples of liquid product and used catalyst.

Catalyst 2A(1) was in the reactor for two weeks with pretreatment taking up 2.5 days at the beginning of the run. Because of its poor performance in the initial stages it was rapidly taken over a range of operating conditions in search of improved performance.

Catalysts 2A-(1) and 2A-(2) were run in parallel for three weeks each. The first 2.5 days were taken up by pretreatment followed by a week and a half of operation at the requested pressure of ~150 psi, followed by operation for 1 week at ~250 psi.

The quantities reported in tables 1-3 should be read with the following understanding in mind:

Duration is the length of time during which the reported sample was collected.

Temperature and pressure are parameters which settle down slowly in our system. In general a change in conditions takes 3

to 6 hours to line out. If a significant change in catalyst performance is induced by a change in conditions the first sample collected after the change is not representative.

Space velocity is reported in Gas Hourly Space Velocity terms and represents the volume of total feed (H_2 + CO) supplied per hour divided by the bulk volume of the pelletized catalyst.

There are two important routes to CO convertion: one leads to the production of hydrocarbons (HC) the other to CO_2 via the watershift reaction. Both are reported here, and the total CO conversion is the sum of the two.

Gasoline and Diesel are defined as C_5 to 220 °C and 220 °C to 340 °C respectively. These quantities are reported as weight percent of the CO converted to hydrocarbons.

The value of $(C_1 - C_4)/C_{5+}$ is a weight ratio of the total yield of light ends to the weight of liquids produced and is a measure of the efficiency of liquid hydrocarbon production.

TABLE 1

Results obtained using 2A(1)

Samp. No.	Date of Start	Durat. hr	Temp. °C	Press. psig	SV h^{-1}	Conv. mol% of CO to HC	Conv. mol% of CO to CO_2	Gaso. wt% of HC	Diesel wt% of HC	$(C_1-C_4)/C_5+$ wt. ratio
1	7/11	24.3	312	150	358	21.2	18.8	2.98	0.29	25.7
2	8/11	50.3	312	150	301	20.3	19.9	8.25	0.32	10.6
3	10/11	21.0	310	150	334	30.2	29.0	9.46	1.16	8.2
Change Pressure										
4	11/11	25.4	315	250	318	32.2	31.4	14.05	0.0	6.1
5	12/11	22.4	311	250	326	31.9	30.7	13.73	0.90	5.7
Change Pressure										
6	No samples taken									
7	13/11	20.9	312	300	307	32.1	33.4	11.42	0.27	7.5
Change Pressure and Temperature										
8	14/11	21.1	319	323	327	25.6	38.4	13.8	1.98	5.26

TABLE 2

Results obtained using 2A-(1)

Samp. No.	Date of Start	Durat. hr	Temp. °C	Press. psig	SV h^{-1}	Conv. mol% of CO to HC	Conv. mol% of CO to CO_2	Gaso. wt% of HC	Diesel wt% of HC	$(C_1-C_4)/C_5+$ wt. ratio
1	Lining out at reaction conditions									
2	5/12	21.2	309	150	315	5.8	3.5	0.0	0.0	0.0
3	6/12	70.8	305	154	275	12.2	12.3	25.1	0.0	3.0
4	9/12	24.0	311	151	333	23.0	13.9	58.1	1.62	0.67
5	10/12	23.4	310	150	321	15.7	16.8	25.4	1.37	2.71
6	11/12	26.2	310	150	314	16.3	18.9	26.2	1.27	2.61
7	12/12	21.5	310	150	312	17.6	20.0	28.4	1.48	2.31
Change Pressure										
8	13/12	79.1	311	256	309	18.1	30.7	18.8	0.79	4.09
9	16/12	17.1	311	258	371	26.5	30.6	65.4	3.09	0.45
10	17/12	23.9	310	250	324	22.4	32.0	33.6	0.94	1.88
11	18/12	25.3	310	255	319	22.0	32.2	32.7	0.77	1.98
12	19/12	23.1	310	250	319	22.3	32.4	31.9	0.92	2.04

TABLE 3

Results obtained using 2A-(2)

Samp. No.	Date of Start	Durat. hr	Temp. °C	Press. psig	SV h^{-1}	Conv. mol% of CO to HC	Conv. mol% of CO to CO_2	Gaso. wt% of HC	Diesel wt% of HC	$(C_1-C_4)/C_5+$ wt. ratio
1	Lining out at reaction conditions									
2	5/12	21.5	312	151	324	5.4	6.7	7.9	0.0	11.3
3	6/12	71.1	307	151	303	9.9	13.9	14.1	0.0	6.0
4	9/12	23.9	308	150	335	14.9	35.7	13.3	0.0	6.4
5	10/12	23.6	310	150	306	10.8	14.5	18.6	0.0	4.3
6	11/12	26.3	310	150	307	11.0	17.4	19.7	0.0	4.1
7	12/12	20.9	310	150	288	12.1	18.4	22.1	1.0	3.3
Change Pressure										
8	13/12	99.1	311	256	304	3.4	41.4	48.5	12.6	0.62
9	17/12	21.1	310	250	335	25.5	29.9	55.9	1.26	0.75
10	18/12	25.4	310	250	305	15.3	32.5	22.6	0.75	3.26
11	19/12	23.3	311	251	307	16.3	31.2	24.6	1.03	2.90

DISCUSSION OF RESULTS

All three catalysts tested showed a prolonged period of activation after the catalyst was put under reaction conditions. During this period gas make in the C_1-C_4 range decreased dramatically while gasoline make went up. This indicates that the initial pretreatment is either ineffective or perhaps counterproductive. In any case, the catalyst does not reach steady state under the first operating condition for some 50 hours. After that, changes in operating pressure take less time to line out.

Catalyst 2A(1) was run at a range of pressures and seems to stabilize in performance at about 250 psig with further pressure increase to 320 psig having less effect. At the high pressure (above 250 psig) the catalyst gave ~65 % conversion of CO, about equally split between CO_2 and HC production. Gasoline selectivity (based on HC production) was ~13 % and diesel ~1 %. The light to heavy HC production weight ratio remained high at about 6.0.

The improved version of this catalyst, 2A-(1) shown in table 2, lined out at 150 psig at ~32 % total conversion again evenly split between CO_2 and HC production. Gasoline selectivity was about 25 % while the light to heavy HC ratio was about 2.5. At ~250 psig this catalyst gave ~55 % conversion again evenly

split between CO_2 and HC make. Gasoline selectivity was much improved, up to the 32 % range while the light to heavy ratio was lowered to ~2. This is a significantly better result than that for 2A(1) at the same conditions and indicates that preparative methods can have a profound effect on catalyst performance. How closely these methods must be controlled is a matter which will require careful and systematic investigation.

An interesting observation can be made regarding samples 4 and 9 in table 2. In both these cases the preceeding run was for a period of 3 to 5 hours (at night) operating at a higher than requested H_2/CO ratio, as high as 1.5 or 2, due to equipment problems. It is very suprising that these two runs gave such excellent gasoline yields and such low ratios of light to heavy hydrocarbons. The results seem to indicate that either a higher H_2/CO ratio should be used in the feed or that the catalyst needs periodic regeneration by a hydrogen rich stream. The results are so promising that a thorough investigation of this phenomenon is indicated.

Catalyst 2A-(2) seems to be less promising than 2A-(1). At standard conditions it gave ~30 % conversion skewed toward CO_2 production by a ratio of ~1.5. Gasoline selectivity was only ~15 % while the light to heavy hydrocarbon ratio was ~4 but decreasing during the whole time on stream. At 250 psi conversion bounced up to ~50 % but the CO_2 production relative to hydrocarbon formation went up to ~2. Gasoline selectivity increased slightly

to -24 %.

An excursion in H_2/CO ratio which occurred before run 8 had remarkable effects on runs 8 and 9 on 2A(2). Not only was the effect as large as that on 2A-(1) (see run 4 in table 2), it was more prolonged. Table 4 summarizes the observed steady state performance as we see it.

TABLE 4

Steady State Performance of Catalyst 2A

	2A(1)	2A-(1)	2A(2)
at 150 psig			
Conversion to HC mol%	21	16	12
Conversion to CO_2 mol%	19	16	16
Total Conversion of CO mol%	30	32	28
Selectivity for Gasoline wt%	8.0	25.0	16.0
Selectivity for Diesel wt%	0.3	1.4	0.0
(Light/Heavy) HC ratio	10.0	2.6	4.5
at 250 psig			
Conversion to HC mol%	32	22	16
Conversion to CO_2 mol%	32	32	32
Total Converstion of CO mol%	64	64	48
Selectivity for Gasoline wt%	13.5	32.5	24.0
Selectivity for Diesel wt%	0.8	0.8	1.0
(Light/Heavy) HC ratio	6.0	2.0	3.0

On the basis of table 4 we can sum up the results as follows:

All three catalysts are of approximately the same activity at 150 psi though at 250 psi it becomes clear that 2A-(2) is less active.

Gasoline selectivity is clearly superior on 2A-(1) at both 150 and 250 psi.

The production of light ends is lowest on 2A-(1) at both 150 and 250 psi.

Under both pressures all three catalysts produce an undesirably large amount of CO_2. This will be reflected in poor carbon economics in any practical application.

Inspection of the products made indicates that the chromatographic product spectra are similar for all catalysts. In cases where material in the diesel range is reported, that material is in the form of a series of paraffins or olefins and associated methyl isomers (we did not identify the molecular species) in a classical FT distribution pattern in the region above the gasoline boiling range. This in itself is very interesting and may give a clue as to the mechanism of the synthesis on this catalyst.

In all three tests when the reactor was shut down and opened the catalyst was found completely encased in a thick mat of coke. In fact catalyst 2A(1) made coke so vigorously that the catalyst basket was distorted by the pressure of the growing coke!

We do not know if the coke was made during pretreatment, during reaction or both. In any case the presence of this material will have severely restricted flow through the catalyst bed, allowing a diffusion limited regime to arise on the catalyst, and forcing serious bypasssing of the bed by the recirculating feed. In view of this we feel that the results reported above are not representative of the real potential of the catalysts tested.

CONCLUSIONS

The observations to date indicate the following:

1) The catalysts tested must be very active to show such large conversions in the presence of such massive coke deposits.

2) The product spectrum can be entirely confined to below the diesel boiling range by a suitable adjustment of operating conditions or procedures.

3) The catalyst seems to be more promising either under higher H_2/CO feed ratios or after periodic regenerations.

4) Too much CO_2 is produced under all the conditions used.

5) Light hydrocarbon product weight can be reduced to below that of the gasoline produced.

6) Catalyst heat treatment before the chemical pretreatment with H_2 and CO has an important effect on catalyst performance.

We conclude that this catalyst would benefit from a long range program of testing and development in order to reveal its optimum commercial potential. In such a program both preparative

methods and reaction conditions should be studied over a wide range.

The results obtained to date only serve to indicate the potential of this catalyst, not its best performance.